Energy Conservation in Textile and Polymer Processing

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FOREWORD

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PREFACE

The polymer-related industries of the United States have developed with the stimulus of low-cost, readily available sources of energy and raw materials from petrochemicals and natural polymers. The emphasis, until recently, has been on obtaining quality desired in the most expeditious fashion with little concern for energy consumed. However, during the past several years energy consumption in preparing and using synthetic and natural polymers has taken on great importance, from the standpoint of both cost and availability. At times industries have been forced to curtail production because of energy shortages, such as the natural gas shortage during the winter of 1976-1977. Consequently, alternate sources of energy have become extremely important. For example, radiation curing might be an attractive alternative to baking in that it substitutes electricity for natural gas. Moreover, the total BTU requirement can be decreased in certain instances by such changes.

The chapters assembled in this volume cover several polymer uses—molded plastics, organic coatings, adhesives, and natural and synthetic fibers. Approaches discussed for conserving energy include redesign of products, reuse of energy and processing materials, reduction in processing temperatures, improvement in equipment efficiencies, development of new polymers, curing, finishing, dyeing techniques, and the most effective use of textiles in indoor habitats. It is hoped that these results and recommendations will stimulate additional research for achieving the nationally important goal of conserving energy and reducing its consumption.

The editors appreciate the support provided by the Cellulose, Paper, and Textile and Organic Coatings and Plastics Divisions of ACS in organizing symposia on this topic and encouraging their publication.

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Progress and Prospects for Energy Conservation in Plastics Processing

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The 15-fold growth of the plastics industry in the past three decades has been based largely on the availability of low-cost petrochemical raw materials for both synthesis and process energy. In the past five years the plastics industry has suddenly become aware that the dwindling supply of petroleum is producing a steady increase in both the cost of plastic materials and the cost of processing them. A recent estimate indicated that process energy was 6% of total production cost; $1.3 billion for U.S. plastics processors in 1976 (1). With the cost of this energy rising rapidly, the urgency of energy conservation is obvious. More optimistically, it has been estimated that plastics processors could use existing technology to save 20-40% of their current energy costs, and thus increase profits 10-20% (1). Long-range future developments could produce much greater savings. In fact, recent studies by DuPont, Exxon, Midwest Research, and Springborn Laboratories all indicate that it takes less petroleum to make and process plastics into finished products than has been required to convert conventional structural materials - such as metals, glass, and paper - into comparable products.

Raw Materials Economics

The prices of petrochemical-based plastic materials must obviously increase steadily. To some extent it is possible to reduce the weight of material needed to make a specific product. Structural foam generally uses 25-50% less material, and often produces equivalent performance. Dow Chemical's Scrapless Forming Process and Shell Chemical's Solid Phase Pressure Forming Process produce higher properties, permitting use of 20-50% less material to form products of equivalent performance (1). Stretch blow molding of bottles produces thinner walls with equivalent performance making it a major current interest.

Recycle of scrap during manufacturing is conventional practice in the thermoplastics industries. At best it may be blended with virgin material and recycled in the same plant, often in the

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same application. At worst it is used at lower value in less demanding products. For example, Western Electric recovers 7000 metric tons/year of PVC from wire and cable insulation by stripping, granulating, recompounding, and converting into cable jacketing, hose, shoes, and mats. The Bell System also recycles 1500 tons/year of ABS from scrapped telephones, uses reground phenolic resin as a filler, and pulverizes DAP scrap for use in virgin DAP molding compounds (2). While such recycle of thermoset scrap poses major problems, current studies indicate that chemical treatment of ground phenolic scrap can make it much more compatible for blending into virgin phenolic molding powders (3).

Even where plastic scrap cannot be reused in plastics processing, it offers high fuel value which can be reclaimed by proper incineration. Wheelabrator has installed a refuse-fired steam-generating plant at Saugus, Massachusetts, which is expected to benefit from the growing proportion of high-energy plastics in solid waste; and 40 more such plants are expected in the U.S. within the next 12 years (2). Rohm & Haas has turned increasingly to burning of combustible solid and liquid wastes for their energy content instead of spending money to discard them (4).

Ultimately non-petrochemical sources of raw materials will become more economical, and synthesis of plastics will turn to these alternate sources, some to produce our present plastics, others to produce new types of plastics. Coal, forestry, and agriculture offer a great variety of interesting opportunities, whenever the economics appear appropriate (5).

Process Technology

As already suggested, redesign can reduce the weight of material needed to make a plastic product. This in turn reduces the amount of energy needed to process it. Redesign of the process can often reduce the amount of scrap which must be recycled, and thus reduce the energy input per pound of finished product. For example, Dow Chemical's Scrapless Forming Process extrudes sheet, which is cut into blanks, warmed in an infrared oven, pressed into preforms with finished edges, and thermoformed into finished parts; improved properties permit use of 20-50% thinner parts, lower temperatures and faster cycles (2-3 seconds) also help, and overall energy saving is 20-30% compared with conventional thermoforming (1). Shell Chemical's Solid Phase Pressure Forming makes polypropylene tubs and trays by heating extruded sheet just below the melting point, clamping over the thermoforming mold, pushing the sheet into the mold with heated plugs, then injecting chilled air through the plugs to force the sheet against the cold surface of the mold; material savings are 40-50%, cycle time is 2.5 seconds, and process energy savings 20-25% (1).

Heat. Thermal energy has proved to be easiest to conserve in plastics processing. Conservation has taken many forms: production, re-use, and reduction of thermal energy.

Production of heat energy at Rohm & Haas has been improved by better control of combustion in boilers, cleaning and maintenance of boilers and process heaters to maintain their efficiency, elimination of steam leakages, steam trap maintenance, and improved condensate recovery (4).

Re-use of heat energy has provided major savings in many plastics processing plants (1,4,6). Mold chillers and hydraulic pump coolers remove tremendous amounts of heat from process equipment. This can be used to heat the plant buildings in winter, using radiators, fans, and ducts to carry the heat wherever it is needed. Applications Engineering Company and Essex International report that use of process heat in this way can supply 67-90% of the heat needed to warm the buildings in winter, so that the heat transfer equipment often pays for itself in the first year of use. During the summer, the fans which cool the chillers are vented to the outdoors, and draw in sufficient make-up air to provide considerable cooling of the buildings, making for greater comfort.

For future plant design, it would be desirable to run exothermic and endothermic processes in parallel lines, so that heat transfer between them would provide optimum economies. In many exothermic polymerization and cure reactions, the heat evolved could be fed back to warm the materials initially up to their reaction temperature, thus recycling the heat energy within a single process. Ultimately, it might even be possible to design exotherm processes which produced more than 100% of their energy requirements, leaving the excess available for sale at a profit elsewhere!

Reduction of processing temperatures would reduce the amount of heat which must be put into a process, and also the amount of cooling which is required afterwards. Goodrich Chemical is designing plastisols which fuse at lower temperatures by use of copolymer resins, lower molecular weights, and solvent-type plasticizers (7). Many plastic processes can be operated at low or even room temperatures, typically the casting of epoxies, polyesters, and polyurethanes. Saum Systems has developed a Displacement Blow Molding system on a 2-station machine operating on a shuttle principle; solid resin is melted and extruded, then a plunger shapes it into a parison, the mold closes around it, and the bottle is blown, with an overall saving of 25% or more in process energy as compared with conventional blow molding (8). MIT surface-chlorinated polypropylene granules, cold-pressed them, used dielectric heating to fuse the low-melting amorphous surfaces together, then allowed the heat to diffuse into the high-melting crystalline interiors, thus eliminating the need for transferring heat in to fuse and then heat out to solidify, and also shortening the molding cycle at the same time (9). On a very mundane level, Rohm & Haas simply reduced the heating level in plant buildings, saving energy without reaching the discomfort level (4).

Power. The high melt viscosity in most plastics processing requires considerable mechanical power both to make the melt flow and to handle the heavy equipment which operates at these high pressures. Power requirements can be reduced somewhat by more efficient operation of the equipment, more drastically by changing to lower-viscosity processes.

Equipment efficiency has been increased in many ways. Craven Wanless and Fabri-Form reduce the power loss in induction motors which start and stop frequently, such as pumps and compressors, by adding extra coils and capacitors to reduce the power factor, saving 15-40% of the energy required to operate them in this way (1). Goodrich has designed an extruder screw with parallel twin flights, a solid channel of constant width and a melt channel of increasing width, thus reducing the number of primary flights in the melting section, and reducing power requirements 25-70% per pound of product (1). Rainville saves 15% of the power used in injection molding and injection blow molding, by rotating the reciproscrew during the injection stage of the cycle (10). Control Process designs instrumentation and control equipment to minimize pump operating time required to fill and pack the mold cavity, thus saving 20-30% of the operating power (11). Combining many such improvements, New Britain Plastic Machine and Reed Prentice report that their new injection molding machines have lower horsepower and higher plasticating and injection rates, requiring 20-75% less power to operate them (1). Clear Shield Plastics saved 8% of their power requirement by converting old plunger-injection machines into screw-injection operation (1). Displacement blow molding, already described above, reduces both heat and power requirements to produce the overall saving of 25% of more in process energy (8). Rohm & Haas also went to delivery trucks with 25% less fuel consumption, and passenger car fleets with smaller wheel base and better gas economy; and plant managers learned to shut down completely any equipment that was not in use, all in the interest of reducing energy consumption (4).

Lower-viscosity processes can make the same product with less power input, and this advantage may eventually become a critical factor in plastics processing. Crystalline polymers melt sharply to low-viscosity fluids, and solidify sharply to rigid products, whereas amorphous polymers soften gradually to high-viscosity melts and solidify gradually on cooling; thus crystalline polymers can often be processed with lower power and shorter cycles. Many structural foam processes operate at low pressure, and in lighter-weight equipment, than solid processes, and thus require less power for processing. Reaction injection molding represents a major trend toward lower power requirements in injection molding, handling low-viscosity liquids instead of high-viscosity melts. Casting processes require little or no pressure, giving energy-saving advantages for plastisols, epoxies, polyesters, and polyurethanes in many applications. Latex coating requires much less power than extrusion coating, and this distinction may be important in some applications.

Services. Aside from the heat and power required in processes themselves, Rohm & Haas has found considerable energy savings can be accomplished in lighting, air conditioning, and heating of buildings (4). High-pressure sodium vapor lamps proved more economical than incandescent lamps. Boiler flue gases were able to replace nitrogen in some processes requiring inert atmosphere. Their overall energy saving over a four-year period reached 14% per pound of product.

Fewer Processing Steps. Engineers have an old rule-of-thumb which doubles the cost for every step in the overall process. While the factor really varies widely from one step to another, the general message is clear: we can save process energy by reducing the total number of steps in the process.

HPM and Johnson Plastics Machinery report that they can use vented extruders, and vented screw plasticators on injection molding machines, to eliminate the pre-drying step required by many plastics, and thus reduce processing costs 5-20% (1).

In the longer-range, it should be possible to catalyze monomer as it is fed into an injection molder or an extruder, polymerize it in the machine, and remove the finished molding or extruded product in a single step. For thin film, it is conceivable to coat a continuous belt with catalyst, pass monomer liquid or vapor over it, and take off finished film at the end of the pass. Many such processes should already be within the joint grasp of progressive polymer chemists and process engineers. The overall saving in process energy could be tremendous.

Cost of Energy

The cost of process energy may depend very much upon the time of day when it is used, the form in which it is used, and geographical location of the processing plant.

When energy requirements fluctuate, power plants must be sized to handle peak loads, resulting in high capital investments which then go under-utilized much of the time. This is true whether a processor generates his own power or buys it from the power company. Using energy in peak-demand periods can account for up to 80% of the total electric bill (1). Conversely, scheduling electrical demand to reduce peak loads can result in great economies (4). Security Plastics reduced their total energy consumption 15% by computer control to avoid peak loads, automatically shutting down air conditioners and chillers for short periods without harm to the process cycle (1). Rohm & Haas learned to refrigerate water during low-demand hours (at night) and store it in insulated tanks, then use it during the day for process cooling during peak-demand hours (4).

As petroleum becomes more costly and less economical as a source of process energy, the plastics industry can turn to a number of alternatives, which in turn may dictate geographical location of processing plants. Hydroelectric power is often most available in mountainous regions not generally used for industrial development; fluid raw materials could be piped up the mountain, processed near the source of hydroelectric power, and finished products shipped back down the rivers, much as the lumber and paper companies have done. Solar power could best be utilized in sunny equatorial desert areas. Tidal power could be used along the seacoast, particularly in those areas having the highest tides. Labor-intensive processing, such as reinforced and laminated plastics, assembling, finishing, and decorating, could best be done in underdeveloped countries, helping to bring them a higher standard of living at the same time. Wherever this creates a wide separation between plant location and ultimate market, low-cost marine shipment would be desirable; optimally, finished plastic products could be packaged in giant plastic bags and simply towed around the world at low cost to span the gap. Most of these concepts are long-range developments, conceived against days of dwindling petroleum supplies, and intended for more permanent stable balance of the economy in a renewable, ecologically sound system.

Conclusions

This collection of recent developments and future suggestions for energy conservation in plastics processing can be divided into those which are ready for immediate use to provide immediate savings, those which require further capital investment, those which require further practical development, and those which require further long-range research to bring them to fruition. Each segment of the plastics industry should evaluate them from that point of view, monitor and modify the list as time goes on, and proceed to implement these energy savings as soon as is practicable. Such progressive practice will help greatly to sustain the successful growth of the plastics industry and its service to mankind.

References

1. F. Eickelberg, Mod. Plastics, 54, (7), 38 (July, 1977).
2. Mod. Plastics, 54, (1), 110 (January, 1977).
3. R.D. Deanin and B.V. Ashar, in press.
4. Rohm & Haas Reporter, 35, (4), 2 (Winter 1977-78).
5. R.D. Deanin, "Renewable Resources for Plastics", Am. Chem. Soc., Chem. Marketing & Econ., April 7-9, 1975.
6. Application Engineering Company technical literature on mold chillers, by E.C. Waters, J.P. Koziol, and others.
7. D.W. Ward, Goodrich Chemical, private communication.
8. Mod. Plastics, 54, (6), 24 (June, 1977).
9. L. Erwin and N.P. Suh, SPE ANTEC, 22, 202 (1976).
10. D. Rainville, Rainville Company, private communication.
11. D.C. Paulson, Control Process Inc., private communication.

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Concepts in Energy Savings in Plastics Processing

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Energy is defined as the capacity to do work. Based on the Carnot cycle, the theoretical energy required to do any form of work is constant. However, due to different efficiencies of various systems, the actual energy required to do the same work can vary depending on the system used. The ever increasing cost of energy has mandated the need to manufacture under reduced energy conditions. Plastics processing is just one manufacturing field where the potential for energy savings is being explored.

Injection Molding Energy Requirements

Energy is required to make injection molding machines do work. The theoretical energy required to produce a given part is constant for a given set of processing conditions. The processing energy is determined by the temperature to which a plastic resin must be raised to deform it whereafter it is injected into the cavity. The energy consists of three forms: 1) Sensible heat - i.e. heat that is used to raise the temperature of the plastic resin from room temperature to its processing temperature; 2) latent heat (if any), the heat that is required to accomplish a phase change such as melting of a semi-crystalline polymer; and 3) the flow energy which is required to inject the material into the cavity. Heats of reaction can be neglected unless one has a thermoset resin. The flow energy is small in comparison to the sensible and latent heat, and one can estimate processing energy requirements from these two forms. Glanvill (1) lists the approximate total energy requirement at the processing temperature for many common thermoplastics.

If all injection molding machines were 100 percent efficient, the energy required to make a part would be constant regardless of the machine used. No machine is 100 percent efficient; however, some systems are more efficient than others. Figure 1 shows a comparison of energy consumption for various injection molding machines as reported by Reed Prentice Company (2). The calculations are based on 20 working days, 24 hours per day, 1 Kw/hp/hour

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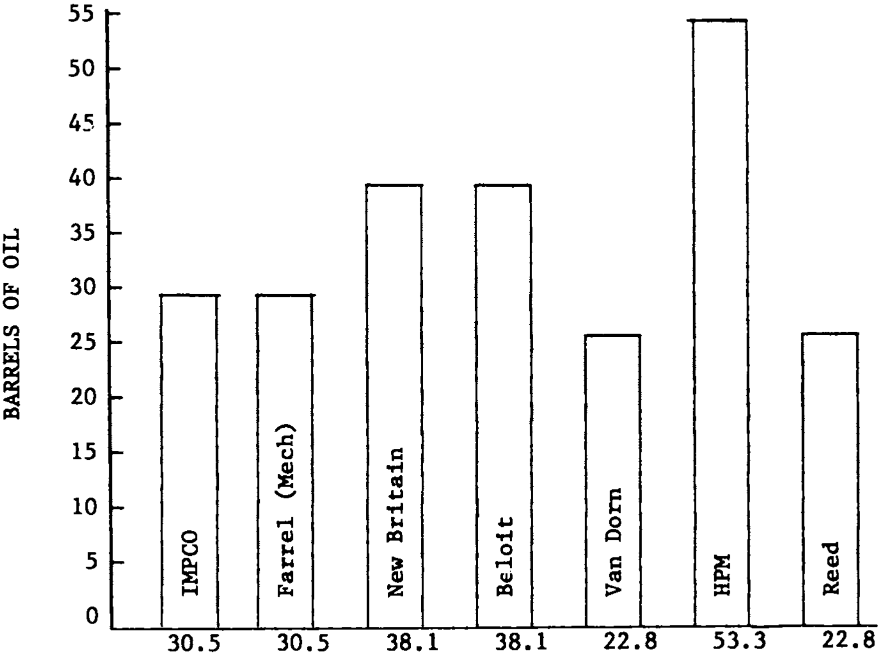

Figure 1. Comparison of plastic injection molding machine energy consumption, 175–225-clamp force (2)

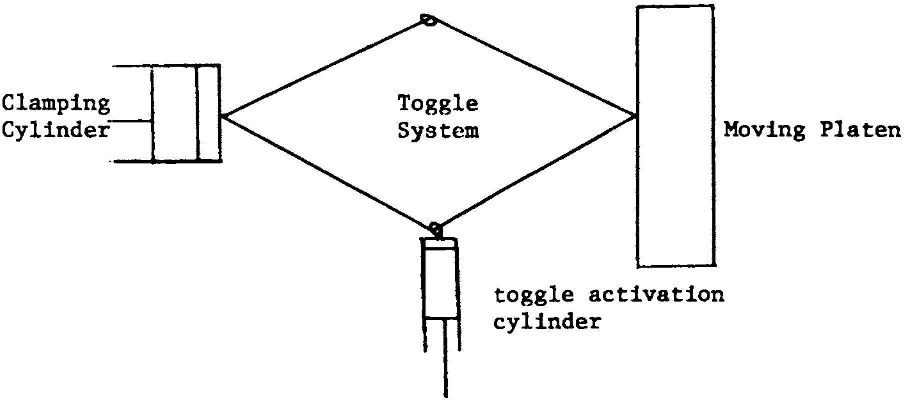

Figure 2. Schematic of hydraulic–mechanical clamping system

and published machine horsepower ratings of manufacturers. A closer examination of these data would show that the high energy consumption machines have hydraulic motors for both the plasticating part of the molding cycle and for the clamping system. If a separate hydraulic motor is used for the clamping system, then energy consumption will be highest. A single hydraulic motor that furnishes energy for both plastication and clamping would be intermediate. The total energy consumption can be minimized if one opts for a mechanical clamping system and a single hydraulic motor. Mechanical clamping systems are commonly used on machines where thin walled parts with very short cycles are molded. A mechanical clamping system has a faster response than a hydraulic system and thus a substantial part of the cycle time can be saved with a fast mold open-close operation. This can also be a disadvantage since the fast mechanical toggle action gives a harder molding closing which decreases the mold life. Hydraulic systems give infinite speed control in closing, extend mold life, but are excessive power consumers for large machines with high clamping tonnages. Large machines operate best when a hybrid clamping system is used. Here one uses large volume, low pressure hydraulics to activate the toggle system and close the mold. Once the mold is virtually closed, a low volume, high pressure system applies the clamping force (see Figure 2).

Motor Selection in Injection Molding

In order to select the most economical drive for an injection molding machine, the duty cycle must be calculated (3). This calculation must be made for each specific application to determine the applicable motor rating. A typical duty cycle is shown in Figure 3. The motor rating is defined in terms of 1) Nameplate horsepower and service factor (SF) and 2) Breakdown torque in terms of full load. One first calculates the RMS HP via Equation (1).

$$\text{RMS HP} = \sqrt{\frac{\Sigma \text{HP}^2\text{T}}{\Sigma \text{T}}} \qquad (1)$$

Table 1 summarizes these calculations for the typical duty cycle shown in Figure 3. The required motor horsepower is given in Equation (2).

$$\text{Required motor HP} = (\text{RMS Load})\ (1.1) \qquad (2)$$

The above relationship allows for a ± 10 percent voltage variation and the particular motor heating, particularly at peak loads at 90 percent voltage. For example (refer to Table 1)

$$\text{RMS HP} = \sqrt{\frac{\Sigma \text{HP}^2\text{T}}{\Sigma \text{T}}} = \sqrt{\frac{118980.38}{52.05}} = 47.8\ \text{HP} \qquad (3)$$

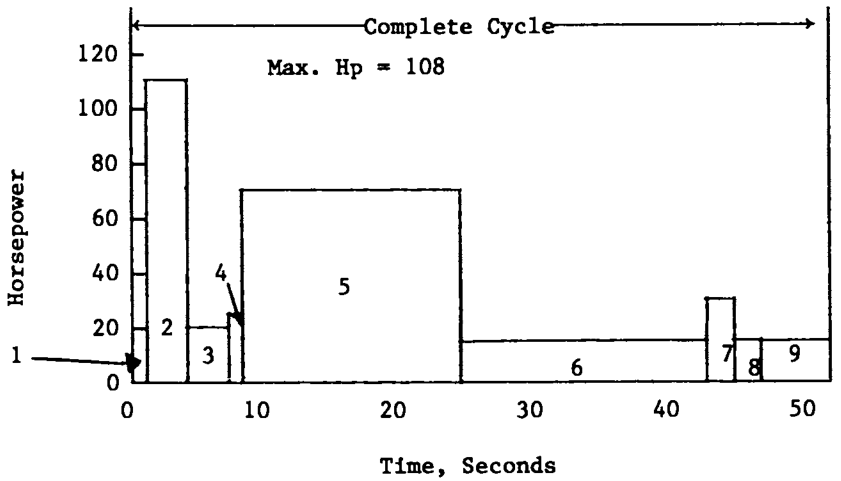

Figure 3. Typical injection molding duty cycle (3)

Table I

Tabulation for Duty Cycle Calculation (see Figure 3) (Ref. 3)

Part of Cycle	Time sec (T)	HP	HP^2T
1	1.5	18.8	530.16
2	4.0	108.0	46656.0
3	3.0	16.0	768.0
4	0.5	18.8	176.72
5	14.8	65.5	63495.7
6	20.0	16.0	5120.0
7	1.25	18.8	441.8
8	2.0	16.0	512.0
9	5.0	16.0	1280.0
	52.05		118980.38

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$$\text{Required motor HP} = (47.8)(1.1) = 52.3\ \text{HP} \tag{4}$$

1) Selecting a 50 HP motor with a 1.15 SF; the usable HP = 50 (1.15) = 57.5 HP
2) Selecting a 60 HP with a 1.0 SF; usable HP = 60 (1.0) = 60 HP

From a thermal viewpoint either rating is suitable for the required load.

Torque requirements must also be considered. The motor must be capable of carrying the peak horsepower (torque) value from the duty cycle at 90 percent voltage. Motor breakdown torque is reduced by the square of the voltage. The relationship is given in Equation (5).

$$\text{Motor \% BDT} = \frac{\text{Peak Load HP x 100}}{\text{NP HP}(.9)^2} = \frac{\text{Peak Load HP x 121}}{\text{NP HP}} \tag{5}$$

For example, using:

1) 50 HP with 1.15 SF:

$$\text{\% BDT} = \frac{108}{50} \times 121 = 261\% \tag{6}$$

2) 60 HP with 1.15 SF:

$$\text{\% BDT} = \frac{108}{60} \times 121 = 218\% \tag{7}$$

A tabulation of prices and ratings would lead one to the proper motor selection. The motor should be sized to operate at high efficiency over the anticipated duty cycle. This allows for a minimum power factor correction. In the low duty part of the cycle, a smaller motor is more efficient. It is strongly recommended that the power factor correction be used to make the motor operate at its peak efficiency over the total cycle. Buyers have a tendency to overspecify the required HP which results in less than peak efficiency.

Utility Requirements in Injection Molding Machines

Actual studies of utility requirements in injection molding were carried out by Olmsted (4). He found that the single greatest expense in operating the machine is the cost of the electrical power. His data show that about half the energy consumed goes into plasticating the resin. Also, his calculations show that the RMS HP rating for the motor is virtually unchanged by the shot size. This means that a smaller motor with special design features to supply high torque requirements to take care of peak loads will do an adequate job (see Table 2). Calculations as presented by Olmsted are usually based on a constant load. Thus, the size of the motor is usually overestimated by 1/4 to 1/3.

Table II

Calculations to Estimate Power Required on an Injection Machine to mold 10 and 4 oz. shots of High Impact Styrene (Ref. 4).

	10-oz shot				4-oz shot			
Machine Action	Pump Pressures^{a}	Cycle Time	Power	(Power)^{2} x time	Pump Pressure	Cycle Time	Power	Power^{2} x time
	psi	sec	hp	hp^{2}sec	psi	sec	hp	hp^{2}sec
Die Close	Screw 0 both 250	1.18	7.3	62.8	Screw 0 both 250	1.18	7.3	62.8
Die Lock	Screw 0 both 1500	0.15	36.4	198.7	Screw 0 both 1500	0.15	36.4	198.7
Ram In	Screw 0 both 1500	1.91	36.4	2530.6	Screw 0 both 1500	0.93	36.4	1232.2
Ram Dwell	Screw 0 small^{c}1500	5.0	8.4	352.8	Screw 0 both 1500	1.0	8.4	70.5
Impulse	Screw 0 both 250	0.2	7.3	10.6	Screw 0 both 250	0.2	7.3	10.6
Screw Return	Screw 2000 small^{c}1500	15.5	25.9	10397.5	Screw 2000 small^{c}1500	6.2	25.9	4159.0
Die Open	Screw 0 both 250	0.97	7.3	51.7	Screw 0 both 250	0.97	7.3	51.7
Hydr. Eject.	Screw 2000 small^{c}1500	1.0	25.9	670.8		0	18.5	342.2
Open Dwell	Screw 0 small^{c}1500	3.0	8.4	211.6	Screw 0 small^{c}1500	1.0	8.4	70.5
Totals		28.91		14487.1		11.63		6198.2

RMS hp = 22.4

RMS hp = 23.1

Olmsted's study showed that other major sources of energy consumption in addition to the electrical motors are the heater bands on the barrel, the scrap grinder motor, the air compressors for general plant use and for hopper loaders, motors in mold chillers, and pump motors and heaters in mold temperature units. Energy savings can be accomplished by running hot runner or runnerless molds. This eliminates to a large extent the regrinding of scrap and eliminates the capital investment in the grinder.

Material Usage Reduction

Substantial energy savings may also be realized by reducing the amount of material that goes into a given part. Part weight reductions greater than 40 percent are possible by proper placement of reinforcing ribs in redesigned parts (5). Weight savings are also realized if one uses structural foam parts. Here the weight reduction is 0 to 30 percent. In each case energy is saved by processing less material and also by saving the inherent fuel value of the material itself.

One Pump Injection Molding Machines

Olmsted concluded in his study that the number and size of the electrical motors could make a sizeable difference in the energy consumption of the injection molding machine. A similar study by Flickner (6) confirms this. He analyzed the energy savings of a one pump injection molding machine. Most conventional systems use two pumps to provide high speed clamp movement, injection and extrusion. However, only one pump is loaded at a time, with the second pump idling. The idling pump becomes an energy waster as it provides no useful work during the idling time. The study shows that an idling pump can draw several horsepower. Figures 4 and 5 illustrate the difference in energy consumption of a one pump versus a two pump system. Figure 4a shows the power consumed when the clamp pump is idling, while the second pump is used for injection and plastification (extrusion). The Kw used during idling are wasted. Figure 4b shows the Kw consumed when the injection pump is idling, while the clamp pump is used for clamp movement. The combined idling Kw of the clamp and extrusion pumps is wasted power. Figure 5 shows the power consumption of a one pump system. The only idling Kw occur during the injection low portion of the cycle, which appear minimal. A comparison of Figures 4 and 5 shows the energy savings of the one pump divert system.

Proper machine cycle settings are also important for energy savings. The injection speed control system (available on new machines as an option or as a retrofit on old machines) optimizes the speeds available for specific time intervals. The injection high volume pump is available for a fixed time period and is then dropped out of the system. This time period should coincide with

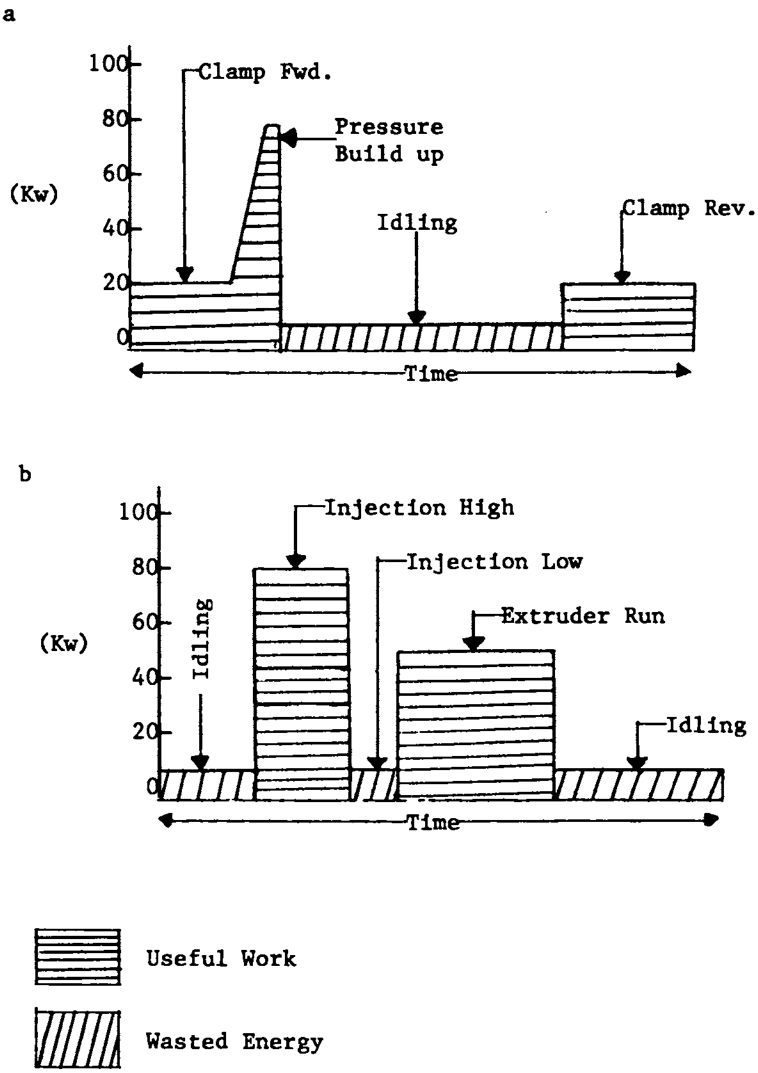

Figure 4. Two pump system: (a) clamp pump, Kw use; (b) injection extruder pump, Kw use

the filling of the part. After the cavity is filled, a pressure control mode takes over which can be held with the injection low volume pump. This eliminates blowing the high volume pump over a relief valve, which is an energy waster. The blowing of pump volume over a relief valve also adds heat to the hydraulic oil. The oil temperature must be kept below 150°F (4) which is the safe operating temperature for pumps. Heat exchangers are provided to cool the hydraulic oil. These require up to 35 gpm for a 400 ton machine. A high water usage becomes an energy waster and adds to the operating costs.

Flickinger (6) states that many operator controls affect the energy consumption of a machine. The heater band controls, if set too high, can waste energy as well as overheat the plastic material, thus delaying cycle time. Keeping the hydraulic oil too cold results in wasting water and leads to increased oil pumping costs since the oil viscosity increases with decreasing temperature. Timer settings need be carefully set so that pumps are not kept under load longer than necessary. Pressure settings should be set as low as possible. Figure 6 shows the relative energy consumption for various conditions of a relative machine cycle (HPM 220 ton machine). It is up to the operator to insure that the above energy conservation procedures be used.

Energy Savings via Stack Molding and Double Shot Molding (7,8)

The preceding discussion has shown that a significant portion of the electrical energy in injection molding is used in the operation of the clamping system. The amount of clamping force is determined by the projected area of the parts and runners. The relationship is:

$$\text{Clamping Force} = (\text{melt pressure})\ (\text{Area}) \qquad (8)$$

By stacking two cavities on top of each other one can mold twice the number of parts with the same tonnage and essentially the same energy consumption for the clamping part. Due to slightly larger runners and slower filling speed per cavity one should actually consider a 15 to 20 percent extra tonnage allowance. Overall one still virtually doubles the output of each machine. Suitable parts to be molded are thin wall parts with large surface area such as overcaps for coffee cans or margarine tubs.

A second energy saving application involves double-shot molding. This technique is used to mold parts that have either different colors of the same material or different materials in the same part. Usually two plasticating units are used with a two cavity mold. The tooling consists of a two cavity mold with the cavities mounted to rotate 180 degrees. Energy savings and labor savings are realized since only one machine and one operator are involved.

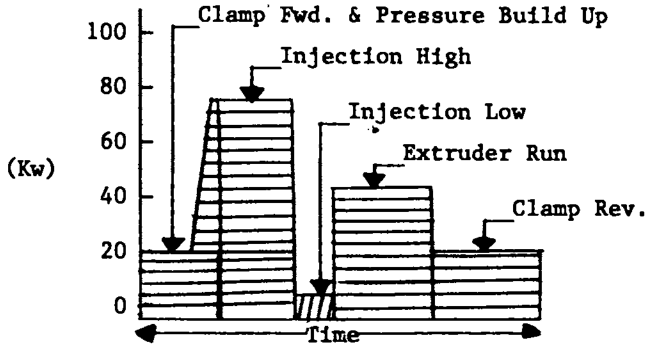

Figure 5. One pump divert system: clamp and injection pump, Kw use

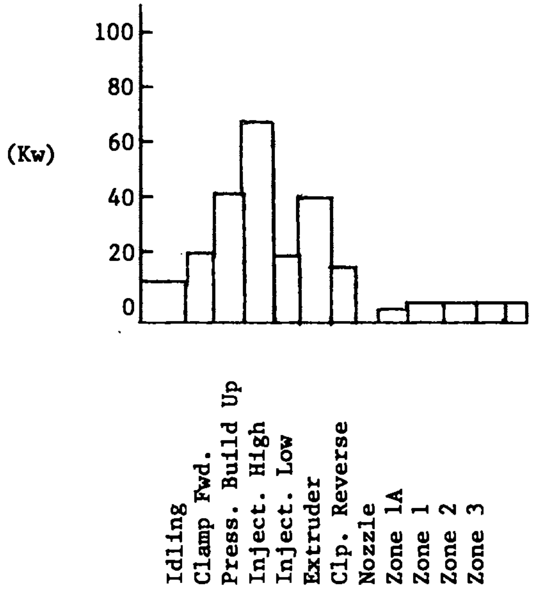

Figure 6. Kw requirement for various conditions during the machine cycle (for total system)

Energy Savings in Drying Operations

Many polymeric materials are hygroscopic and pick up atmospheric moisture which must be removed by drying prior to processing. Calland (9) calculated the energy that is required for drying most thermoplastic resins. These data have been compared with the processing energy that is reported for injection molding in Glanvill (1). The data are presented in Table 3. The energy consumed in drying can represent 1/3 to 1/2 of the total processing energy. However, because of heat losses in the dryer to the surroundings, the drying efficiency is assumed to be only 50 percent (10) and the actual drying energy is equal to the processing energy.

Table III

Typical Processing and Drying Energy Requirements for Thermoplastics (Ref. 1 and 9).

Material	Processing Energy (Btu/100 lb/hr)	Drying Energy (Btu/100 lb/hr)
ABS	14,000 to 17,000	5460
Acrylic	12,500	5120
Acetal	18,000	6143
Acetate	12,500	5120
Butyrate	12,000	6485
Nylons	27,500 to 32,500	15,358 for Nylon 6
		12,970 for Nylon 66
		9,215 for Nylon 610
		7,508 for Nylon 11
		4,780 for Nylon 12
Polycarbonate		6,826
LD Polyethylene	25,000 to 30,000	8,191
Polyethylene with Carbon Black		10,239
Polypropylene	25,000	7,167
Polyimide		6,484
Styrene	12,000	4,095
PVC	7,000 to 15,000	3,754
SAN	12,000 to 15,000	4,788

One can see that the elimination of the drying operation represents a large potential energy saving. As a first step, one can use a hopper dryer so that pellets that are at the elevated drying temperature are fed to the machine. This eliminates the heat loss to the surroundings which occurs in tray dryers. Drying may be eliminated entirely in certain instances as described in two recent developments. HPM (11) has developed a vented injection molding machine which devolatilizes the melt through a vent port similar to vented extrusion. The drying step is eliminated and the energy is saved. Lord (12) reports a second method that eliminates drying. He has shown that certain molds can be modified in their venting systems and pressurized to prevent the formation of splay marks (the moisture of undried resin that wants to come out of solution as the pressure in the mold cavity is released). He found that pressurizing the cavity with N_2 or CO_2 up to 50 psig was effective for molding undried ABS material.

Recovery of Waste Heat

A final thought concerns the energy savings associated with the recovery of waste process heat for space heating purposes. In injection molding the heat removed from the mold by the chiller water is usually lost to the surroundings. This waste heat can be used to heat injection molding plants as reported by Haas (13). The waste heat is recovered in a heat pump type water chiller and blown into the factory area. A similar system has been developed for other commercial installations as reported by Waters (14).

Conclusions

The preceding discussion has shown that energy savings in plastics processing are possible in the area of machine modification, new process machinery, processing operation of the machine itself, and in the area of weight reduction by part redesign and foaming of the resin.

Literature Cited

1. Glanville, A.B., Plastics Engineer's Data Book, p. 20, Industrial Press, New York (1971).
2. Reed Prentice Bulletin, Package Machinery Co., East Longmeadow, MA 01028.
3. G.E. Bulletin GEP-363, General Electric Company, Schenectady, New York.
4. Olmsted, B.A., Modern Plastics, p. 31 (March 1966).
5. Crate, J.H., Engineering Design with DuPont Plastics, E.I. DuPont De Nemours & Co., Wilmington, Del. 19898.
6. Flickinger, W., "Energy Saving, One Pump Divert Systems", in HPM Now, (Fall 1977), HPM Corp., 820 Marion Road, Mount Gilead, Ohio 43338.
7. Husky Newsletter, (Feb. 1978), "Stack Mold Developments", Husky Injection Molding Limited, P.O. Box 1000, Bolton, Ontario, Canada LOP 1A0.
8. Sesko, R.F., Plastics Machinery and Equipment, 7, 43 (June 1978).
9. Calland, W.N., SPE ANTEC, 17, 306 (May 1971).
10. McLeod, John, "The Drying of Hygroscopic Thermoplastics", Bulletin by Thoreson-McCosh, Inc., Troy, Mich. 48084.
11. DeCapite, R., and C.S. Gudermuth, "The Vented Reciprocating Screw Plasticator", HPM Corporation, Mt. Gilead, Ohio 43338.
12. Lord, H.A., SPE ANTEC, 24, 83, Washington, D.C., (April 1978).
13. Haas, N., SPE J. 23, No. 2 (Feb. 1967).
14. Waters, C.E., Applications Eng. Corp., Elk Grove Village, Ill.

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Energy Efficiency in Plasticating Screw Extrusion

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The most widely used polymer conversion processes are injection molding, extrusion, blow molding, thermoforming, calendering and compression molding. All of these processes consist of basically three functional steps (Figure 1); plastication or melting of a polymer solid, forming of the polymer melt into a desired shape and solidification of the formed polymer article.

Forming is accomplished by pressure or other types of stress and requires only a small amount of mechanical energy, insignificant in comparison to the energy required for melting. Solidification is accomplished by cooling the polymer melt for thermoplastic polymers, and by curing and subsequent cooling for thermoset polymers. At present, the polymer processing industry does not recover the thermal energy removed from the polymer melt by cooling. The melting step consumes the major portion of energy required for processing and the energy efficiency in this step is regrettably low. Melting is accomplished by the thermal energy from the equipment's heaters and more importantly by the viscous dissipation of mechanical energy from the equipment's motor. Both the heaters and the motor are usually powered by electricity. Since polymers have a very low thermal conductivity, melting by external heating is inevitably a slow process giving a low production rate. However, a large amount of heat can be generated internally in polymers by viscous dissipation of mechanical energy because of the high viscosity of polymer melts and thus melting by mechanical energy is a fast process giving a high production rate. Melting is accomplished in all modern processes primarily by mechanical energy. We will define in this paper "the mechanical energy efficiency" as the amount of polymer melted per unit mechanical energy consumption of the drive motor.

Screw extruders (Figure 2) are used to melt polymer solids in most major processes. Almost all thermoplastic polymers are extruded at least once, often twice or more, before their final products are made. The trend in the last two decades has been ever-increasing speed and size of extruders in order to obtain higher production rates with almost no concern for energy efficiency.

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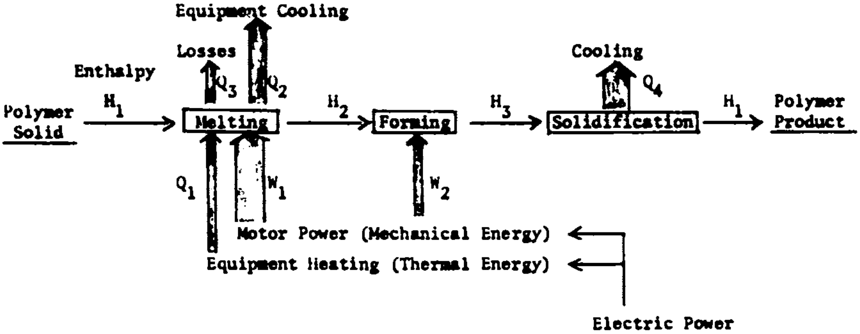
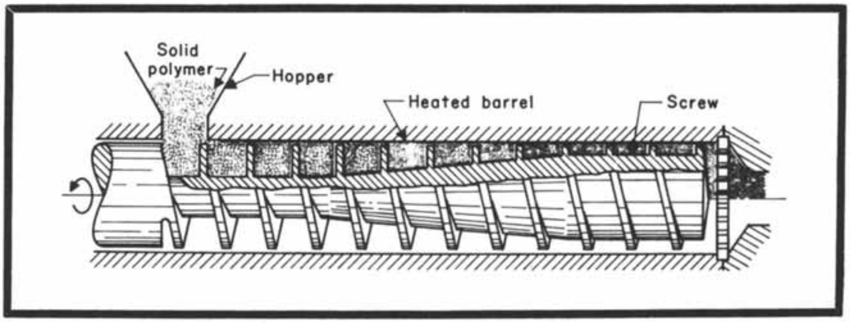


Figure 1. Functional steps and energy flow in a typical polymer process



Plastics Engineering

Figure 2. Schematic of an extruder

In Energy Conservation in Textile and Polymer Processing; Vigo, T., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 1979.

In fact, many modern extruders generate enormous quantities of excess heat and they are equipped with high capacity cooling systems to remove the excess heat, which would otherwise increase the melt temperature to an undesirably high value or even degrade the polymer. Consequently, the energy efficiencies of the modern extruders have decreased substantially although the production rates have increased. For example, a 2.5 in. (63.5 mm) diameter extruder about 20 years ago usually had a length to diameter ratio of 20 and produced 50-70 kg/hr operating at 50-100 RPM at the mechanical energy efficiency of 5-7 kg/kw-hr of the motor power. Today, a 2.5 in. (63.5 mm) diameter extruder usually has a length to diameter ratio of at least 24, often 30, and produces 70-100 kg/hr operating at 100-150 RPM at the mechanical energy efficiency of 4-6 kg/kw-hr, a decrease of about 1 kg/kw-hr from that 20 years ago. Assuming that the entire energy for melting is provided by the motor and no energy is lost, the theoretical maximum mechanical energy efficiency in extrusion processes based on the enthalpy difference (H_1-H_2) between a polymer solid at room temperature (1) is 6-10 kg/kw-hr or 8 kg/kw-hr on the average for most large volume polymers such as polyethylenes, polypropylene, polystyrene, polyvinyl chloride and nylons. Thus, 5 kg/kw-hr on the average with modern 2.5 in. (63.5 mm) diameter extruders represents only 62% mechanical energy efficiency. The mechanical energy efficiencies with larger extruders are even worse.

The total sale of major thermoplastic polymers in the United States was reported at approximately 10 million metric tons in 1977 (2). Taking an average 50% mechanical energy efficiency of 4 kg/kw-hr at present and two-path extrusion, about 5 x 10^9 kw-hr of electric power should have been consumed to process these polymers in 1977. In terms of fuel value, this represents about 49 x 10^{12} BTU/year (taking three times the electric figure). At an assumed 75% mechanical energy efficiency of 6 kg/kw-hr which should be possible, only about 33 x 10^{12} BTU/year of fuel would have been used to process these polymers. Thus, a large amount of fuel equivalent to 16 x 10^{12} BTU/year could have been saved according to this estimation. The actual energy saving by improved energy efficiencies of extruders in the entire polymer processing industry could be many times this amount. The world polymer production in 1973 was approximately 43 million metric tons (3) and thus a tremendous opportunity exists worldwide to save energy in polymer processing. Additionally, a better understanding of the conversion processes will lead to materials savings by reducing scrap in processing. Currently, 2 $\sim$ 3% of all polymers become scrap during processing due to overheating and other adverse process reasons.

Energy efficiency has not been a real concern to the polymer processing industry until recently. However, the cost of energy is fast becoming an important factor in polymer processing. Also, the pressing energy problems in the United States and around the world have created a growing concern about energy efficiency in

In Energy Conservation in Textile and Polymer Processing; Vigo, T., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 1979.

the polymer processing industry. A number of articles (4, 5, 6, 7) on this subject have appeared recently in the trade journals.

Melting in Screw Extruders

Solid polymer in the form of pellet or powder dropped into the screw channel from the hopper is compacted into a solid plug due to the screw rotation and the solid plug is forced to rub on the heated barrel surface. The solid plug is plasticated or melted in screw extruders primarily by the mechanical energy provided by the drive motor rather than the thermal energy from the heated barrel.

An idealized melting mechanism in screw extruders is shown in Figure 3. When the solid plug is rubbed on a heated barrel surface, a thin layer of melt or melt film develops between the solid plug and the barrel surface. The melt film exchanges heat with the barrel surface and also generates heat by dissipating the work done by the motor in rubbing the solid plug on the barrel surface. A large amount of heat can be generated in the melt film owing to the very high viscosity of polymer melts, and it has been generally believed that the melt film temperature can become higher than the barrel temperature requiring barrel cooling in high speed operations.

Melting occurs primarily at the solid plug/melt film interface due to the heat flux (q) from the melt film into the solid plug. The mass rate of melting per unit interface area (Ω) will be proportional to q.

$$\Omega \propto q \tag{1}$$

The rate of work done (W) on the system by the screw per unit interface area is the product of the stress (τ) and the rubbing velocity (V_b).

$$W = \tau \cdot V_b \tag{2}$$

The mechanical energy efficiency (ε) of the drive motor can now be expressed by the ratio of Ω to W.

$$\varepsilon = \frac{\Omega}{W} = \left(\frac{\Omega}{V_b}\right)/\tau \propto \left(\frac{q}{V_b}\right)/\tau \tag{3}$$

Conceptually, q can be calculated from the temperature profile in the melt film and τ can be calculated from the velocity profile in the melt film. Then, it should be possible to calculate the mechanical energy efficiency according to Equation 3 and predict the temperature, velocity, and pressure conditions necessary for the maximum mechanical energy efficiency. The concept for calculating the mechanical energy in melting is straightforward and easy to understand as described above. However, the real trouble in calculating the mechanical energy efficiency comes from

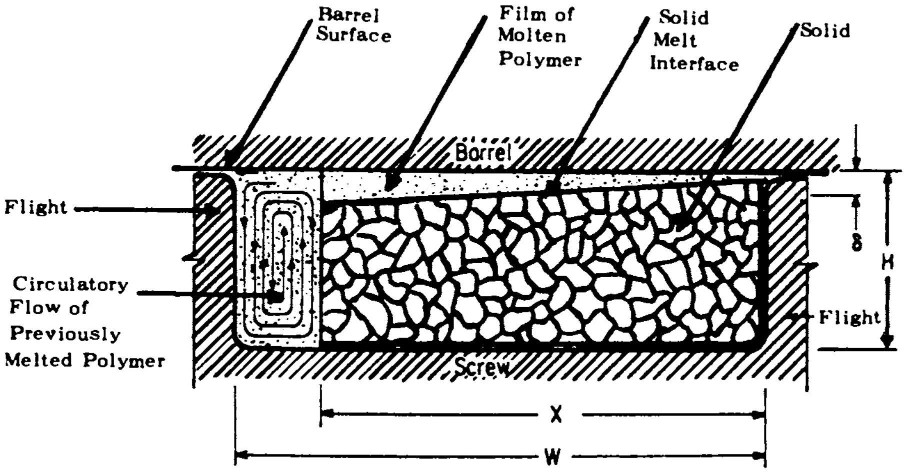


Figure 3. Idealized cross section of a screw channel

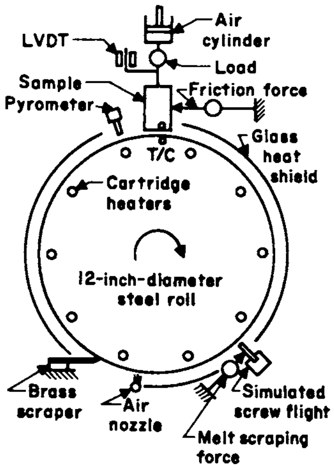
the difficulty of calculating the temperature and velocity profiles in the melt film. Since a polymer melt is highly pseudoplastic as well as highly viscoelastic, the mathematical equations describing the actual temperature and velocity profiles in the melt film become extremely complex and the analytical solutions for these equations cannot be obtained (8).

Experimental Results and Discussion

Special equipment called "Screw Simulator" was constructed as shown in Figure 4, which can be used to study the melting mechanism of polymers on heated, moving metal surface. The Screw Simulator basically consists of a heated, 12-inch (30.48 cm) diameter steel roll rotated by a 5 HP-DC motor, a sample holder, an air cylinder to press the sample against the rotating roll, a brass blade to remove the polymer melt from the roll surface, and a number of electronic control and monitoring instruments. It is designed to control independently three primary operating variables (temperature, pressure and speed) in the range comparable to actual processing conditions. Also the sample width can be changed. The maximum temperature and speed of the roll are approximately 800°F (425°C) and 40 in/sec (100 cm/sec), respectively. The maximum load on the sample is 12,500 lbs (5,675 kg) and the maximum sample size is 3 in^2 (19.35 cm^2). The rate of melting (Ω) is measured by a LVDT connected to the shaft of the air cylinder. The sample holder is mounted on two bearings and free to rotate in the direction of the roll rotation. The stress (τ) between the polymer sample and the roll is measured by a strain gage which is mounted to impede any movement of the sample holder.

Using the Screw Simulator, Ω and τ for the seven commercial polymers listed in Table I were measured as a function of the roll surface temperature (T_b), and the roll velocity (V_b). T_b corresponds to the barrel temperature of extruders and V_b approximates the peripheral screw speed. All polymers were molded into 1-inch (2.54 cm) cube samples and all measurements were made with the molded samples at room temperature. Although the use of molded samples does not directly represent the actual extrusion processes which take polymer pellets or powders, it assures full contact with the roll surface and thus simplifies the theoretical analysis of the experimental data and the comparison to theoretical predictions. The mechanical energy efficiency (ε) was calculated from the experimentally measured Ω and τ values according to Equation 3. The primary objective of the investigation to date has been to examine the validity of the present melting models in predicting Ω. The values of ε were calculated for the purpose of this paper from the available experimental data taken for other purposes. Therefore, a high accuracy in the ε values reported in this paper is not expected.

Figures 5-11 and 12-18 present ε as a function of T_b and V_b, respectively. A solid line is drawn in each figure representing



Modern Plastics

Figure 4. Schematic of screw simulator

TABLE I List of Polymer Samples

Polymer	Source	Melting Temperature (°C)	Glass Transition Temperature (°C)
HDPE	Phillips Petroleum	132	--
LDPE	Exxon Chemical Co.	110	--
PP	Exxon Chemical Co.	165	--
POM	Celanese	166	--
PS	Foster-Grant	--	100
PMMA	Rohm and Hass	--	105
PC	General Electric	--	150

HDPE = High Density Polyethylene
LDPE = Low Density Polyethylene
PP = Polypropylene
POM = Polyoxymethylene
PS = Polystyrene
PMMA = Polymethylmethacrylate
PC = Polycarbonate

the maximum mechanical energy efficiency (ε_m) that can be achieved when the energy from the motor is used without any loss to heat the polymer from room temperature to the roll surface temperature. ε_m depends only on T_b neglecting the small influence of pressure on enthalpy. Experimental values of ε greater than ε_m indicate that the polymer melts by the heat conducted from the heated roll surface as well as by the mechanical energy from the motor. In this case, the polymer melt is not heated above T_b and no energy is lost. Experimental values of ε less than ε_m indicate that the polymer melt is heated above T_b by the mechanical energy from the motor and thus the roll surface must be cooled to maintain its temperature, resulting in energy loss. Assuming that the polymer melt eventually attains the roll surface temperature by exchanging heat with the roll, the maximum energy efficiency (combining the mechanical energy from the motor and the thermal energy from the heater) will be achieved at the roll surface temperature where experimental ε crosses ε_m.

Referring to Figures 5-11, it is found that ε increases with T_b and that ε can be substantially less than ε_m at low processing temperatures. ε becomes greater than ε_m only at relatively high processing temperatures. From these experimental results, ε is expected to increase with increasing barrel temperature in actual extrusion operations as far as the melting mechanism is concerned. Excessive mechanical energy can be consumed resulting in overheated melt when the barrel temperature is kept too low. Polycarbonate (PC) in Figure 11 shows a maximum ε at about T_b = 210°C but ε increases with T_b in the usual processing range above 230°C. This maximum is associated with a transition in the adhesive property of PC on the metal surface (9).

Figures 12-18 show that ε initially decreases very sharply with increasing V_b to about 30 cm/sec and then decreases slowly beyond V_b = 30 cm/sec. It is noted that modern extruders are usually operated at high speeds above V_b = 30 cm/sec. ε is much greater than ε_m at very low V_b indicating that the energy for melting comes mainly from the heated roll by conduction. ε becomes almost the same as ε_m at high V_b for all polymers even at high T_b. One can expect from this finding that the entire energy for melting is provided by the motor in all high speed extrusion operations. In such cases, the energy consumed by the screw flight to scrape off the molten polymer from the barrel surface and to pump out the polymer melt collected in the melt pool will cause overheating and give a low energy efficiency. Additional mechanical energy often is required in extrusion to mix various feed components. This additional energy consumption, although not wasted, also contributes to overheating.

Conclusions

The experimental results with molded polymer samples show that the mechanical energy efficiency in melting solid polymers by

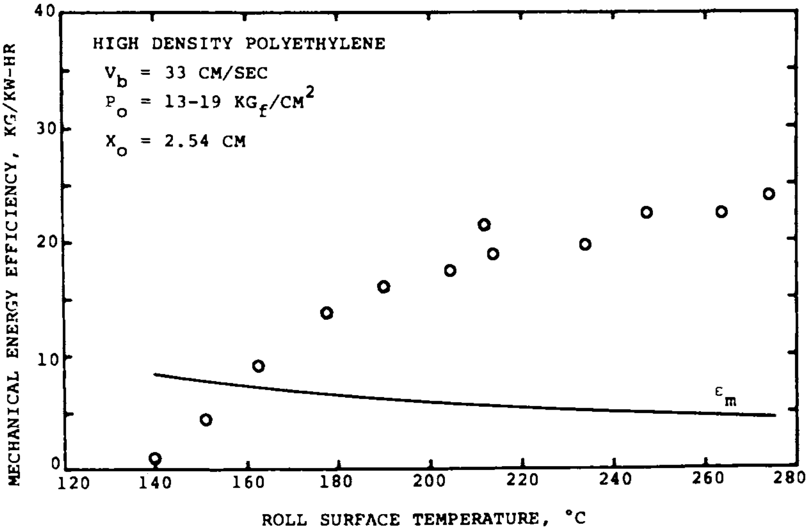


Figure 5. Mechanical energy efficiency as a function of roll surface temperature for high density polyethylene

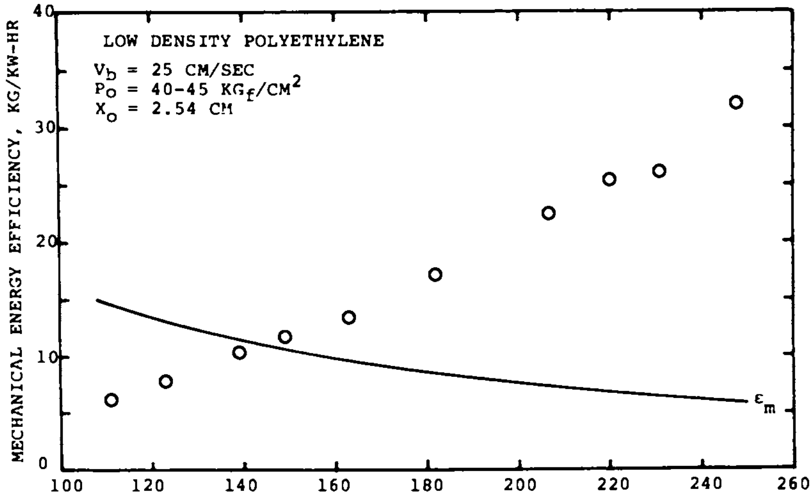


Figure 6. Mechanical energy efficiency as a function of roll surface temperature for low density polyethylene

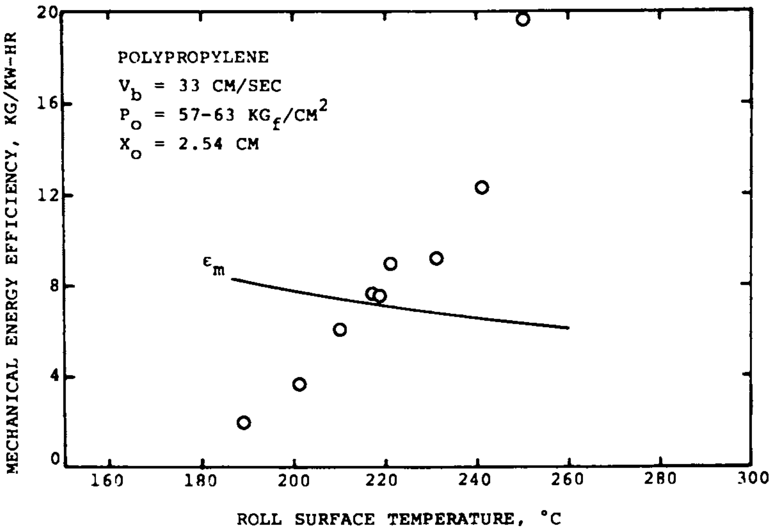


Figure 7. Mechanical energy efficiency as a function of roll surface temperature for polypropylene

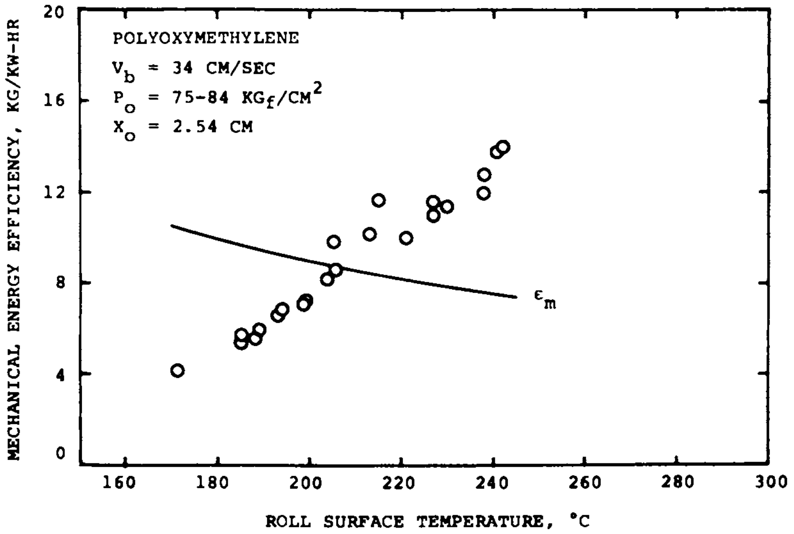


Figure 8. Mechanical energy efficiency as a function of roll surface temperature for polyoxymethylene

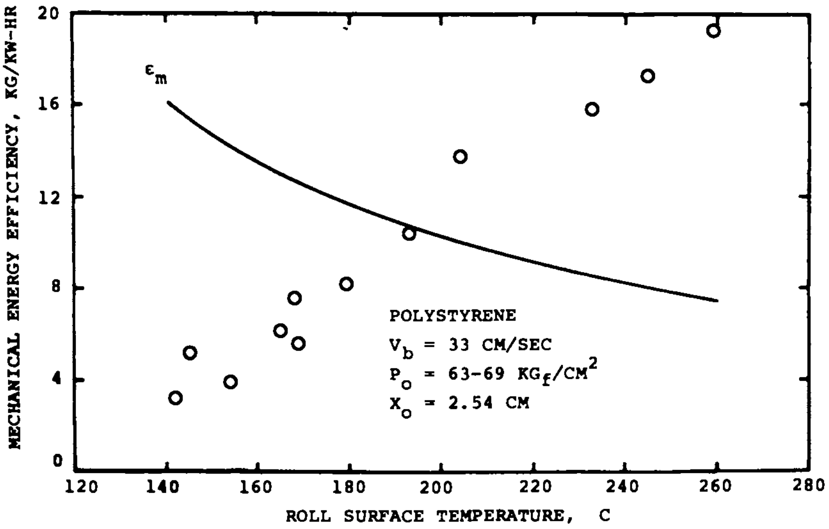


Figure 9. Mechanical energy efficiency as a function of roll surface temperature for polystyrene

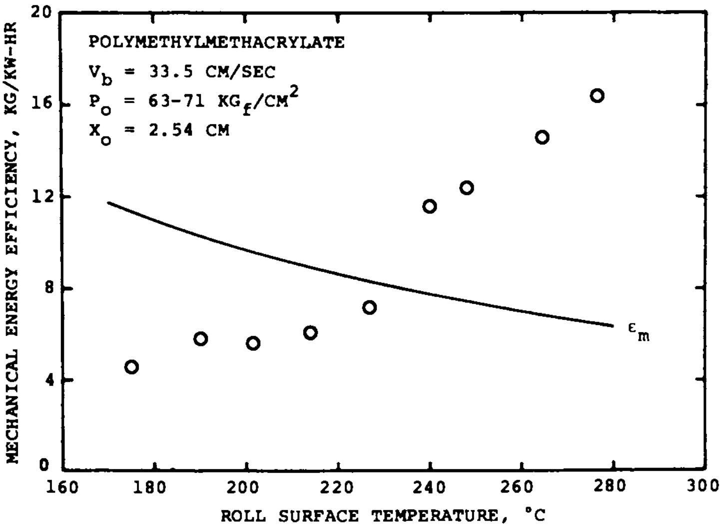


Figure 10. Mechanical energy efficiency as a function of roll surface temperature for polymethylmethacrylate

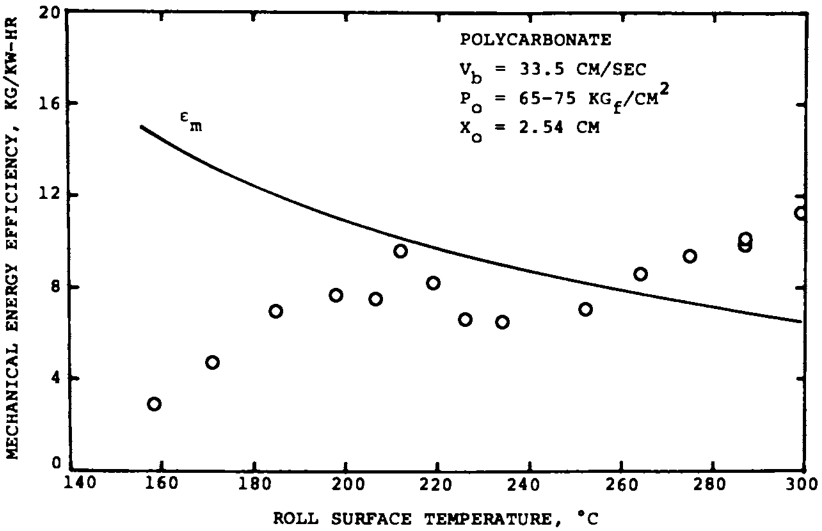


Figure 11. Mechanical energy efficiency as a function of roll surface temperature for polycarbonate

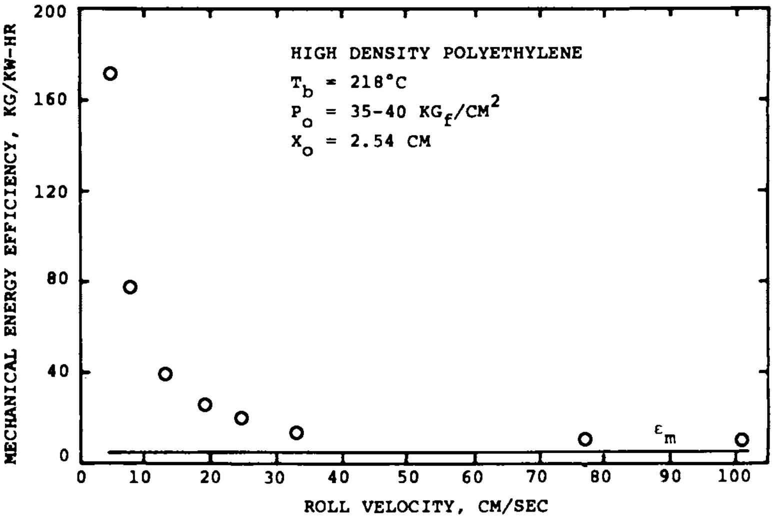


Figure 12. Mechanical energy efficiency as a function of roll velocity for high density polyethylene

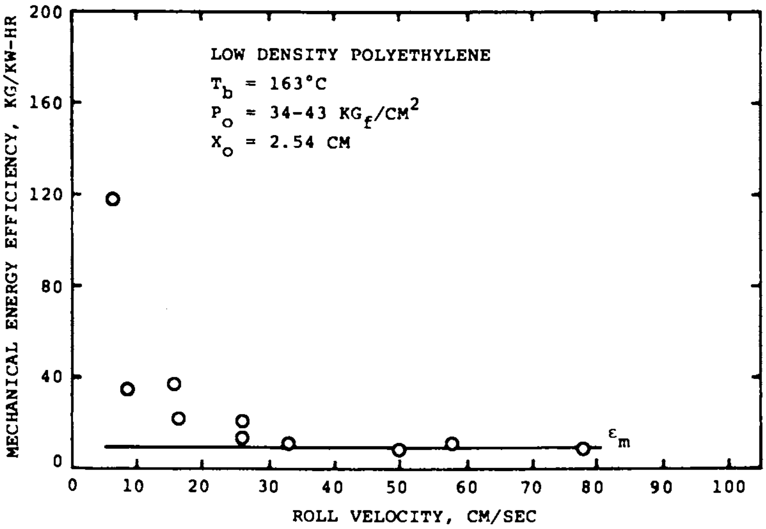


Figure 13. Mechanical energy efficiency as a function of roll velocity for low density polyethylene

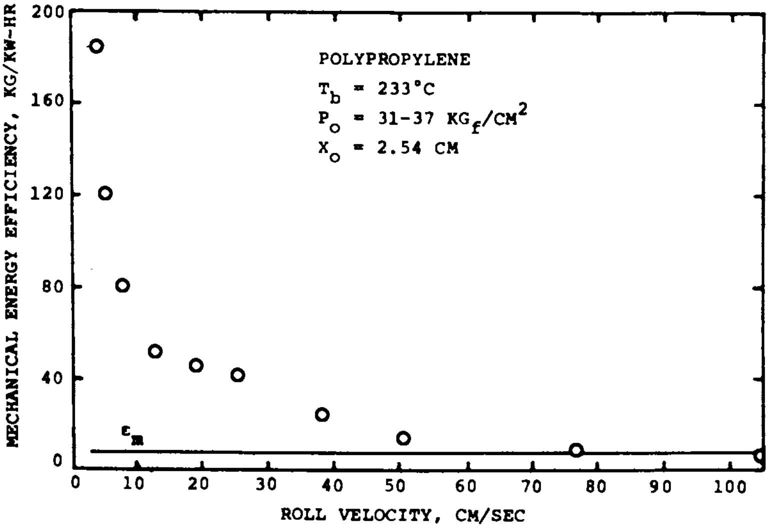


Figure 14. Mechanical energy efficiency as a function of roll velocity for polypropylene

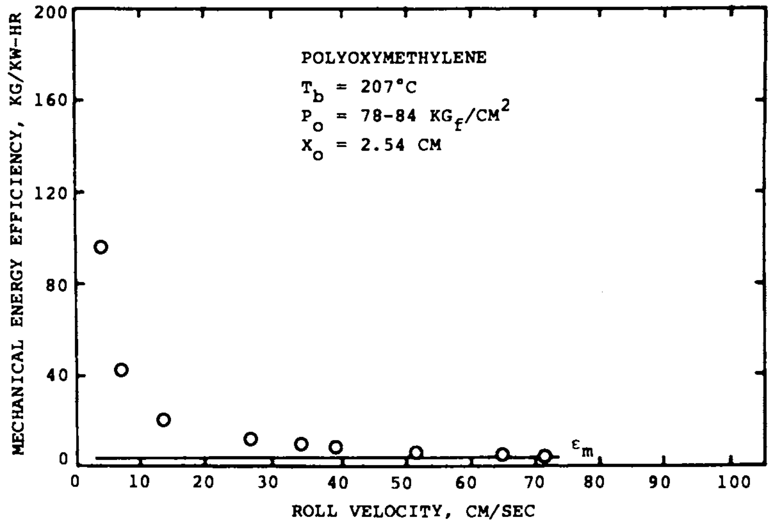


Figure 15. Mechanical energy efficiency as a function of roll velocity for polyoxymethylene

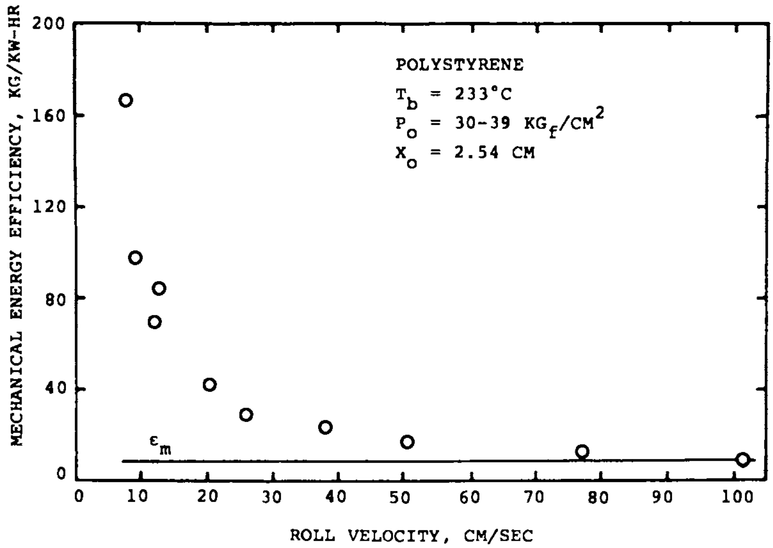


Figure 16. Mechanical energy efficiency as a function of roll velocity for polystyrene

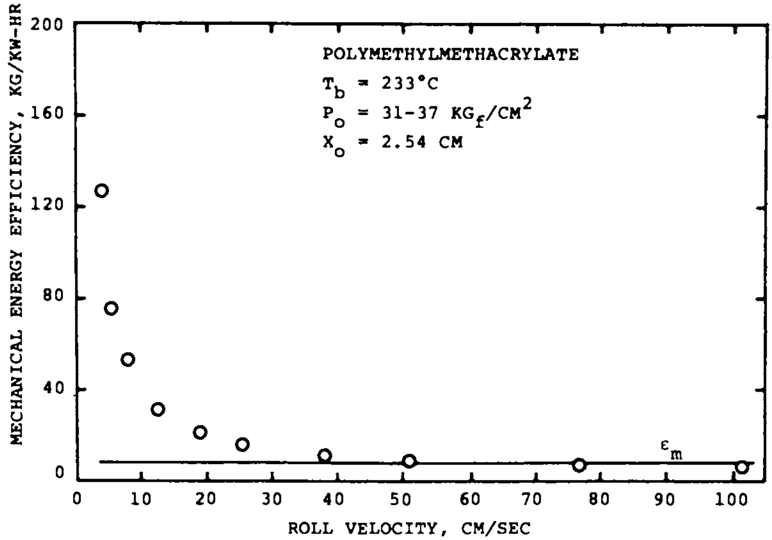


Figure 17. Mechanical energy efficiency as a function of roll velocity for polymethylmethacrylate

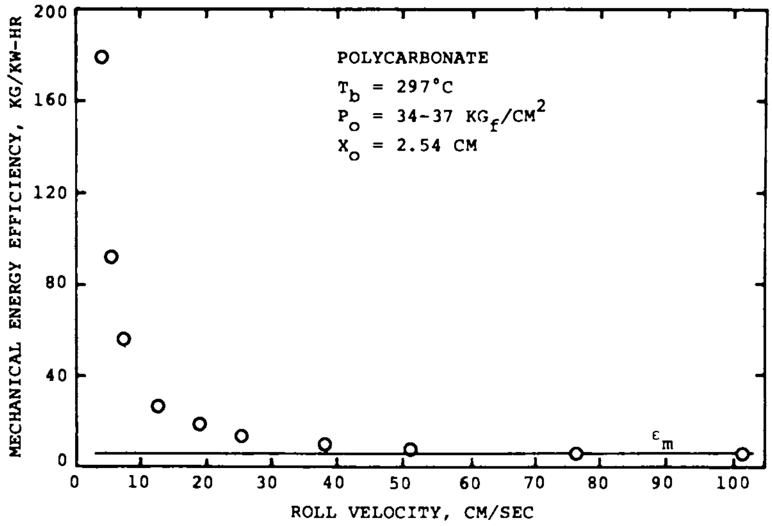


Figure 18. Mechanical energy efficiency as a function of roll velocity for polycarbonate

rubbing on a heated metal surface increases with increasing metal surface temperature and decreases with increasing rubbing velocity. At low metal surface temperatures and high rubbing velocities, the melting mechanism by itself consumes excessive mechanical energy from the motor, much more than necessary to heat the polymers from room temperature to the metal surface temperature. The melting mechanism at high rubbing velocities always consumes enough mechanical energy to heat the polymers from room temperature to the metal surface temperature even at high metal surface temperatures. Therefore, high screw speed extrusion operations at low barrel temperatures will overheat the polymers above the barrel surface temperature, requiring barrel cooling, just by the mechanical energy of the motor consumed in rubbing the polymer solid on the barrel surface. The polymer melt will be heated even higher by the additional mechanical energies consumed by the screw flight and other flow requirements. This can explain why most modern extruders must be operated with barrel cooling.

All experimental results reported in this paper were obtained with molded samples for a theoretical reason. These experiments should be repeated with pellet samples so that the experimental results could be more directly applied to actual extrusion operations. The energy efficiency will become an important factor in the future in designing a new extruder for a given output rate as energy cost increases.

Acknowledgement

It is gratefully acknowledged that our extrusion research was sponsored by the National Science Foundation.

Literature Cited

1. Bernhardt, E. C., "Processing of Thermoplastic Materials," Reinhold (1959).
2. Modern Plastics, 55(1), 49 (1978).
3. Platzner, N., Chem. Tech., 5, 103 (Feb. 1975).
4. Mack, W. A., Plastics Engineering, 29(11), 31 (1973).
5. Bauer, L. R., Plastics Technology, 48 (June 1974).
6. Waters, C. E., Plastics World, 56 (Dec. 1974).
7. Plastics Technology, 11 (May 1974).
8. Pearson, J.R.A., Imperial College Polymer Science & Engineering Group, Report Nos. 4 and 5 (1974); J. Heat and Mass Transfer, 19, 405 (1976).
9. Mount, E. M., III and Chung, C. I., Poly. Eng. Sci., 18(9), 711 (1978).
10. McClelland, D. E., M.S. Thesis, RPI, December 1977.

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Energy Conservation Through Silicone Liquid Polymer Processing System

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Fabricated silicone rubber parts are traditionally made from high consistency silicone gum stock. Because of the stiffness of the gum stock, the material must be worked with rubber masticating equipment and preformed before fabrication. A new fabricating process using a low consistency liquid silicone rubber was introduced by Dow Corning Corporation recently (1,2,3). This process is called liquid polymer system (LPS).

Prior to the introduction of the LPS process, the low consistency liquid silicone rubber was not considered for use in fabricated parts because of the inadequate physical properties. Recent advancements in the low consistency silicone elastomer technology, however, have led to the development of high strength material. The property profile of silicone rubber thus obtained is now comparable to that of high consistency silicone rubber. This is shown in Table 1.

The LPS process offers a variety of manufacturing advantages over the conventional fabricating process. Primarily, benefits are seen in the reduction of capital investment and labor costs, (1,2) pollutants, waste material and energy requirements. The energy conservation by the LPS process is especially important and attractive in view of today's worsening energy situation.

The purpose of this paper is to demonstrate a fabricator's energy savings through the use of the LPS process compared to a conventional process using a high consistency silicone gum.

Results and Discussion

Injection Molding. LPS is a completely automated process. Once the liquid components are introduced to the feed system, the material is pumped, mixed, molded, demolded and collected without manual handling. Energy intensive equipment such as mills, extruders and heavy duty presses normally used in rubber processing are replaced with air pumps, motionless mixers and lightweight injection molding machines. This results in considerable energy savings. Schematics illustrating the LPS system and a conventional

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high consistency molding operation are shown in Figure I and II respectively.

TABLE 1. Comparison Of Typical Liquid Silicone Rubber With
A Typical High Consistency Silicone Rubber

	Liquid Silicone Rubber		High Consistency Silicone Rubber
	Silastic® Q3-9590	Silastic® Q3-9595	Silastic® 4515U
As Supplied Property			
Solid Content (%)	100	100	100
Viscosity	Pourable(a) Pumpable	Pumpable(b)	Gumlike
Physical Properties(c)			
Durometer (Shore A)	35	48	52
Tensile Strength [M Pa (psi)]	5.5(800)	7.6(1,100)	7.6(1,100)
Elongation (%)	450	350	540
Tear,Die B,KN/M(ppi)	15.8(90)	31.6(180)	17.5(100)

Note: (a) 1,000 poise
(b) Extrusion Rate at 90 psi through 1/8" orifice=150 g/min
(c) Vulcanization Condition
  (a) Silastic® Q3-9590 and Silastic® 4515U : 5 min at 150° C + 4 hrs post cure at 250°C
  (b) Silastic® Q3-9595 : 5 mins at 150°C

To demonstrate the actual savings realized by a fabricator, the energy required to mold a 9 gram spark plug boot by the LPS process and by the conventional process is compared. In this calculation, it is assumed that 100% acceptable parts are produced by both processes. In practice, the rejection rate of LPS is much lower than the conventional process. The results of calculation are summarized in Table II. The ratio of energy required by the LPS process to that of the conventional process is almost 1:4.

The energy cost of materials in KWH per part can be misleading if the useful life of the products being compared is significantly different. Because of the environmental controls placed on the automobile industry, the under hood temperature have risen significantly. At these high temperatures, which can reach 450°F, the service life of a silicone spark plug boot is at least two and one half times that of a comparable organic boot. The fact that a silicone spark plug boot has this longer service life would make it a better choice than the boot made from organic elastomers. For example, assume that an organic boot (a) has an energy requirement equivalent to that of conventional process, i.e., 0.0536 KWH per boot and lasts 40,000 mile (4 years). A silicone boot molded from a high consistency gum (b) has an energy cost of .0536 KWH per boot, while a boot molded by LPS process (c) has an energy

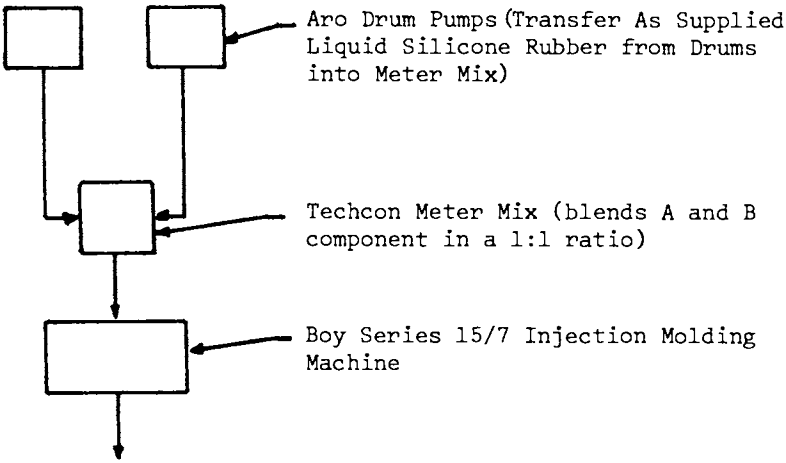

Figure 1. Liquid injection molding for a two component system

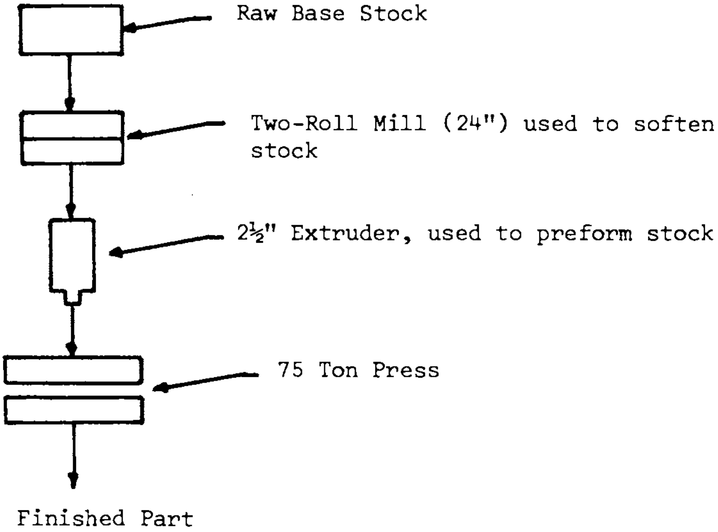

Figure 2. Transfer press molding for a high consistency silicone system

TABLE II. Case No. 1 Energy Consumption For Silicone Spark Plug Boot Production, LPS Process vs Conventional Process

LPS Process		Conventional Process	
Equipment	Energy (KWH)	Equipment	Energy (KWH)
2 Aro Drum Pumps 130cc/CFM at 80 psi	.001	24" 2-Roll Mill (.425 hrs operation)	9.724
1 Meter Mix Pump	.001	2.5" Extruder (30 lb/hr)	4.833
Boy Injection Molding Machine Series 15/7		75 ton Krass Transfer Mold Press	
Motor	6.6	Motor	7.000
Heater(50% duty)	1.0	Heater(50% duty)	4.180
Total	7.602	Total	25.737
Spark Plug Production Rate (4 cavity mold, 24 sec cycle time) = 600 parts/hr		Spark plug production rate (40 cavity mold, 5 min cycle time) = 480 parts/hr	
Energy comsumption per Spark plug boot (KWH)	.01267		.0536

TABLE III. Case No. 2 Energy Consumption For Three Gram Silicone Parts, LPS Process vs Conventional Process

LPS Process		Conventional Process	
Equipment	Energy (KWH)	Equipment	Energy (KWH)
2 Aro Drum Pumps 130 cc/CFM at 80 psi	.0004	2-Roll Mill(14.92 KW) 5 min/8 hr shift	.1554
1 Meter Mix Pump	.0004	Transfer Mold Press	
Boy Injection Molding Machine Series 15/7		Motor	6.3840
Motor	6.60	Heater(50% duty)	4.5000
Heater(50% duty)	1.00	Total	11.0394
Total	7.6008		
Production Rate			
4 cavity mold, 20 sec cycle time	720 parts/hr	59 cavity mold 5 min cycle time	708 parts/hr
Energy Consumption per part (KWH)	.01055		.01559

cost of .01267 KWH. Both silicone boots have a useful service life of 100,000 miles (10 years). Thus (a) requires .0134 KWH per

In Energy Conservation in Textile and Polymer Processing; Vigo, T., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 1979.

year per boot, (b) .0054 KWH per year and (c) has an energy cost of .0013 KWH per year per boot. This is a fourfold energy savings over high consistency silicone and a tenfold savings when compared to high consistency organics. Table III shows an actual case history for molding a three gram rubber article. Even though the conventional process involved little mechanical performing, the data still shows an energy savings by using the liquid polymer injection molding concept. Additionally, the amount of waste was reduced from 48% in the conventional system to 10% in the liquid polymer system.

Extrusion Coating - The use of liquid silicone rubber in coating application requires less energy than conventional dispersion coating processes. Solventless material, rapid cure time, absence of by-products and the elimination of multiple passes all contribute to the reduced energy demand of the liquid polymer system.

One area in which this technology is making inroads is in the manufacture of conductive ignition core. Schematics comparing this system for producing a silicone conductive core (Figure 3) to the solvent dispersion method traditionally used (Figure 4) are shown.

The following criteria were used in determining the energy requirements needed to fabricate a silicone conductive core.

1. Actual production runs have shown that the footage of core produced with the LPS system is double that of the dispersion system.
2. Actual energy calculations are based on a pilot scale vertical oven which is six feet in length. The maximum footage produced in this system was 50 feet per minute using the liquid silicone conductive core material. Production runs exceed this figure by a large percentage.
3. The diameter of the uncoated core is 75 mils and the thickness of the coating is 5 mils.

Actual energy (KWH) used in the manufacture of one million feet of conductive core are shown in Table IV.

If one takes into consideration energy required to vaporize the solvent in the dispersion process, further energy savings can be realized. This is theoretically calculated using the following data: (a) core diameter = 75 mils, (b) coating thickness = 5 mils (c) dispersion composition = 22% solid, 78% xylene, (d) specific heat of silicone = 0.3 cal/g/°c and heat of vaporization of xylene = 93.4 cal/g, (e) output speed: 120 ft/min by LPS process and 60 ft/min by dispersion process and (f) cure temperature: 110°C by LPS process and 204°C by dispersion process respectively. Results of calculation are shown in Table V. A 20-fold energy savings could be realized in a system designed exclusively for the LPS system.

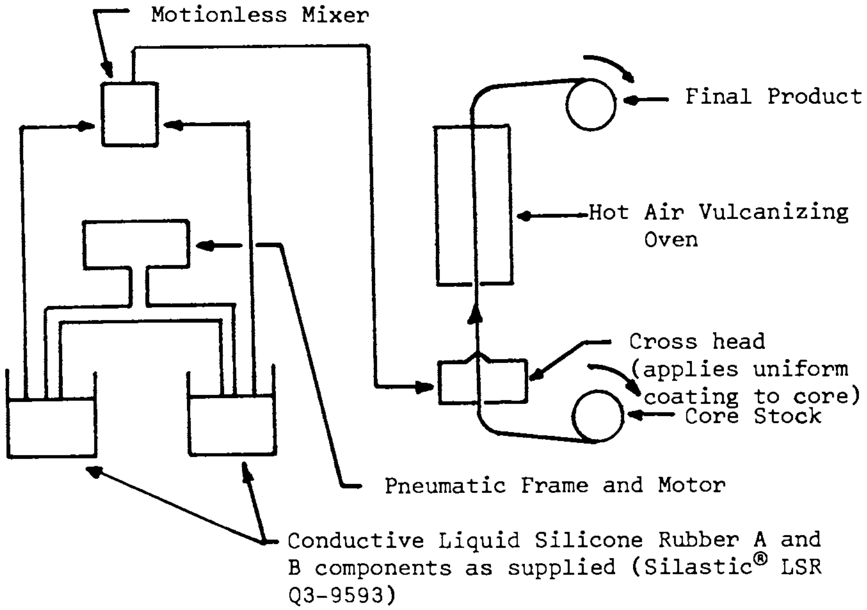

Figure 3. Conductive core coating by LPS process

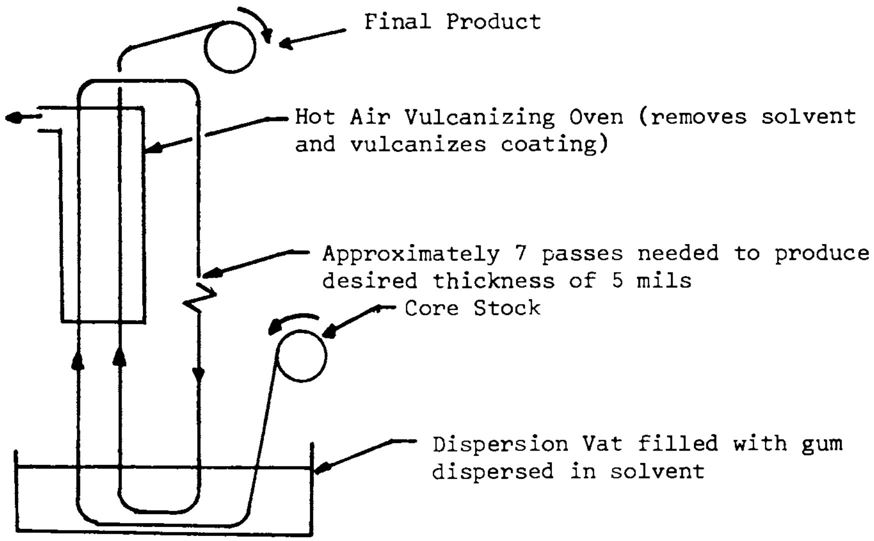

Figure 4. Conductive core coating by solvent dispersion process

TABLE IV: Comparison Of Energy Consumption For Coating Conductive Core With Liquid Silicone Rubber vs Silicone Rubber Dispersion

	Required Energy (KWH)	
	LPS Process	Dispersion Process
2 Drum Pumps 130 cc/CFM at 80 psi	.001	
HAV Oven		
Motor	.7	.7
Heater*	10	10.0
Conveyor Motor	.37	.37
Total (KWH)	11.071	11.07
Conductive Core (ft/min)	50	25
KWH per ft	.00369	.00738
KWH per M̄ ft	3,690	7,380

*50% duty time

TABLE V: Calculation Of Energy Required For Conductive Core Coating, LPS Process vs Solvent Dispersion Process

	LPS Process	Dispersion Process
Weight of Coated Rubber	32 g/min (120 ft/min)	17.18 g/min (60 ft/min)
Removal of Xylene		
Weight of xylene (g/min)		60.9
Energy required (k cal/min)		8.5
Energy required to cure rubber coating (k cal/min)	0.8	0.9
Total Energy Required (K cal/min)	0.8	9.4
Energy Consumption per 100 ft of core (K cal)	0.67	15.67

Future Use of LPS Process - Other potential areas where the LPS process can be employed are sleeving, fabric coating, roll covering, encapsulation, thin wire coating, tubing, and wire jacketing and insulation. As technology develops, energy savings will be realized in these fabrication applications through the elimination of milling, preforming, and solvent and by-product removal.

Summary - A means of saving energy by using a new fabricating process, LPS, for injection molding and extrusion coatings has been presented. Actual data shows a significant energy savings for the LPS process over conventional processes.

A more basic way of viewing this energy savings is by relating the energy saved to the electrical energy needed to operate a private residence. Assume 100 $\bar{M}$ spark plug boots were produced in the United States last year. The use of the LPS system would save 4,093,000 KWH. Based on figures obtained from Consumers Power Company of Michigan, that's enough power to electrically operate 682 homes for one year.

Acknowledgement

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Literature Cited

1. Kehrer, G. P., and Hays, W. R., Paper presented at the 16th Annual TLARGE Foundation Tech. Conf. Univ. of South Calf., Los Angeles, Calf., June (1977).

2. Hays, W. R., Kehrer, G. P., and Monroe, C. M., Paper presented at the 112th Meeting of the Rubber Div., Am. Chem. Soc., Cleveland, Ohio, Oct. 4-7 (1977).

3. Kehrer, G. P., and Monroe, C. M., Paper presented at the Passenger Car Meeting, Society of Automotive Engineers, Detroit September 26-30 (1977).

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Microwave Curing of Silicone Elastomers and Foams for Energy Savings

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When dielectric materials are heated by microwave, the heat generated, P, is given by the following equation (1)

$$P = 0.555\ f\ \varepsilon^2 E' \tan\delta \times 10^{-6}$$

Where f = frequency
ε = field strength
E' = dielectric constant
$\tan\delta$ = loss tangent

For a given f and ε, the heating efficiency is directly proportional to E' and $\tan\delta$. The product of these two parameters is called the loss index, ε''. Loss index of 0.2 or more results in good heatability; 0.08-0.2, fairly good heatability; 0.01-0.08, poor heatability; and under 0.01 there is little or no response (2).

The loss index of silicone elastomers made from polydimethylsiloxane, generally speaking, is low due to their low values of dielectric constant and loss tangent. The dielectric constant of polydimethylsiloxane is almost independent of the frequency, whereas the $\tan\delta$ is highly dependent on the frequency in the microwave region (3,4). At 3×10^9 Hz, a 1000 cs polydimethylsiloxane fluid has a $\tan\delta$ of about 0.0096 and a dielectric constant of 2.76. This gives a loss index of 0.0264, which puts polydimethylsiloxane in the poor heatability category.

One can, however, increase the loss index of silicone polymers by increasing either E' or $\tan\delta$ of the material. This can be done in two ways, i.e.,

A. Changing the structure of the silicone polymer.
B. Introduce an additive, which has a high loss index.

In the former approach, the loss index can be increased by changing the substituents on silicone. Vincent et al (5) reported that as the R group in $Me_3SiO(MeRSiO)_xSiMe_3$ was changed from methyl to a bulky polar group, the dielectric constant and loss factor increased drastically. This is shown in Table I.

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TABLE 1. Effect Of Chemical Composition On The Dielectric Constant E' and Tan δ Of $Me_3SiO(MeRSiO)_xSiMe_3$(a)

R	E'		tan δ	
	100 Hz	1,000 Hz	100 Hz	1,000 Hz
$-n-C_8H_{17}$	2.38	1.38	<.00001	<.00001
$-n-C_4H_9$	2.54	2.54	.00017	.00002
CH_3-	2.76	2.76	<.00001	<.00001
Ø-	3.03	3.04	.00027	.00003
H-	3.18	3.18	.00001	.00001
$Cl(CH_2)_3-$	6.84	6.84	.0038	.0005
$CF_3(CH_2)_2-$	6.84	6.84	.0014	.00063
$p-NO_2-C_6H_4-$	19.28	18.85	.078	.01

(a) Reproduced from 1972 Annual Report, Conference on Electrical Insulation and Dielectric Phenomena, page 17, with the permission of the National Academy of Sciences, Washington, D.C.

National Academy of Sciences

Theoretically, therefore, silicone polymers containing bulky polar substituents should have higher loss index and hence can be heated by microwave much more efficiently than polydimethylsiloxane. In practice, this approach can be pursued in two ways, namely, (a) blending or (b) copolymerization. In the former case, polydimethylsiloxane is blended with a high loss index polymer, $(MeRSiO)_x$, at the ratio which gives the desired heatability without sacrificing other physical properties. In the latter case, one can make a random or block copolymer, i.e., $ViMe_2SiO(Me_2SiO)_x(MeRSiO)_ySiMe_2Vi$, where R is the bulky polar group described above. Ratio of y/x determines E' and tan δ (5) and hence ε" and heatability of the resulting copolymer.

In the additive approach, the loss index is increased by placing a high-loss material in contact with a low-loss material. The high-loss material heats and transfers its heat to the low-loss load. Some examples of such additives are carbon black in rubber, NaCl in urea-formaldehyde glue for wood and polyvinylchloride in polyurethane foam (2).

The purpose of this work is to demonstrate the feasibility of curing silicone elastomers and foams by microwave based on the theoretical prediction presented above. The frequency and field strength were kept constant at 2450 $\bar{M}$ Hz and 1 KW respectively during the entire course of this work.

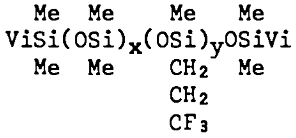
Results and Discussion

Various materials formulated from polymers containing structural units of $Me(CF_3CH_2CH_2)SiO$, $Me(HSCH_2CH_2CH_2)SiO$,

$ClCH_2CH_2CH_2MeSiO$, and ethylene oxide respectively were used to demonstrate the concept of microwave curing (6). Results are summarized below:

Methyltrifluoropropylsiloxane Containing Elastomer. A two-part sealant formulation shown below was employed.

Part A:

Parts	
100	 $$\mathrm{Vi}\underset{\mathrm{Me}}{\overset{\mathrm{Me}}{\mathrm{Si}}}(\mathrm{O}\underset{\mathrm{Me}}{\overset{\mathrm{Me}}{\mathrm{Si}}})_x(\mathrm{O}\underset{\substack{\mathrm{CH_2}\\ \mathrm{CH_2}\\ \mathrm{CF_3}}}{\overset{\mathrm{Me}}{\mathrm{Si}}})_y\mathrm{O}\underset{\mathrm{Me}}{\overset{\mathrm{Me}}{\mathrm{Si}}}\mathrm{Vi}$$ (Polymer I) random copolymer, x/y = 1/1, 1,959 cs., %Vi = 0.28%
30	Reinforcing silica
0.5	Pt Catalyst
0.5	Fe_2O_3

Part B:

Parts	
100	Polymer I
30	Reinforcing Silica
3.39	Curing Agent (SiH containing compound)

Part A and Part B were mixed at weight ratio of 1:1 and placed in a microwave oven and 1 KW energy was applied. The temperature of the mixture reached about 150°C in 3 min and crosslinking reactions took place. The elastomer thus obtained had deep section uniform curing all the way through. The same type of curing was obtained in the absence of Fe_2O_3.

The crosslinking reaction responsible for curing in this system is the hydrosilation shown below:

$$\equiv SiH + ViSi\equiv \xrightarrow{Pt} \equiv SiCH_2CH_2Si\equiv$$

Although the curing of sealant based on the reaction shown above takes place at room temperature, the rate of curing can be accelerated by heating the sealant to 100-150°C, using a conventional oven or a hot press molding device. In the present case, the curing reaction obviously was accelerated by the heat generated by the microwave heating.

Mercaptopropyl Containing Elastomer

Part A:

Parts	
100	Vinyl endblocked polydimethylsiloxane (Polymer II)
25	Minusil
30	Luperco CDBM (35% 2,4-dichlorobenzoylperoxide in dibutyl phthalate and Minusil)

Part B:

Parts	
100	$Me_3SiO(Me_2SiO)_{242}(MeHSCH_2CH_2CH_2SiO)_{13}SiMe_3$ (Polymer III)
25	Minusil

Part A and Part B were mixed at a weight ratio of 1:1 and the mixture was placed in a microwave oven (1 KW, 2450 $\bar{M}$ Hz) for 5 min. The material cured to give an elastomer with a dry surface.

At the same time pure Polymer (III) was also placed in the same microwave oven for 5 min in the absence of peroxide and Minusil. The polymer became hot but did not cure at the end of 5 minutes.

These two experiments demonstrate that the heat generated by the microwave decomposes the peroxide to give radicals, which initiate simultaneously the crosslinking reaction shown below (7,8).

$$\equiv SiCH_2CH_2CH_2SH + CH_2{=}CHSi\equiv \rightarrow \equiv SiCH_2CH_2CH_2SCH_2CH_2Si\equiv$$

$$\equiv SiCH_2CH_2CH_2SH \rightarrow \equiv SiCH_2CH_2CH_2SSCH_2CH_2CH_2Si\equiv$$

Chloropropyl Containing Copolymers. Copolymer (IV), consisting of 60 mole % Me_2SiO and 40 mole % $ClCH_2CH_2CH_2SiO_{1.5}$, was placed in a microwave oven at 1 KW input. At the end of 5 min the copolymer became very hot (>100°C). This means that if the copolymer is used to formulate an elastomer along with a curing agent one should be able to cure the sealant with microwave.

Ethylene Oxide Containing Copolymers. The following copolymers were placed in a microwave oven for 5 minutes.

(1) ABA block copolymer, where A is $(CH_2CH_2O)_x$ and B is $(Me_2SiO)_x$, M.W. = 2400 and A:B = 85:15.

(2) $Me_3SiO(MeRSiO)_2(Me_2SiO)_3SiMe_3$ where R = $-CH_2CH_2CH_2OCH_2CHMeOH$.

Both fluids became very hot (>100°C) at the end of 5 minutes. In the case of (2), the material evaporated so fast that smoking was detected.

Additive Approach. As mentioned previously, dimethylsilicone compounds respond poorly to microwave heating because of the low "loss index". To make the dimethylsilicone compounds respond to microwave, one can change the structure of polydiorganosiloxane as shown above, or introduce additives which have a high "loss index" such as carbon black. The latter was demonstrated by applying microwave (2450 $\bar{M}$ Hz) to a mixture of 10 g of base (consisting of 100 pts polydimethylsiloxane and 30 pts of Minusil) and 1 g of carbon black. The mixture became very hot in 5 minutes. In such a case the carbon black could function as a reinforcing agent as well as an additive for improving the microwave heating.

The additive approach also was shown to be effective in making a silicone foam. Kittle and Ronk (9) demonstrated that addition of ferric oxide or alcohols to platinum catalyzed foam formulation would allow the material to foam when heated by microwave, whereas the same composition without ferric oxide or alcohol did not foam or cure.

Summary. Microwaves have been employed successfully to heat and subsequently cure silicone compositions to give elastomers and foams. Microwaves were found to be responsible for heating the silicone polymers and the heat, thus generated, was responsible for the curing. In order for a silicone polymer to be heated efficiently, it should contain some substituents [e.g., $-CH_2CH_2CF_3$, $-CH_2CH_2CH_2SH$, $-CH_2CH_2CH_2Cl$ or $-(CH_2CH_2O)_x$] which cause an increase in the dielectric constant and/or tan δ of the silicone polymer such that the "loss index" of the system can be increased drastically. Another approach to the heating and curing of silicone composites by microwave is to introduce an additive which has a high loss index, such as carbon black, Fe_2O_3 and alcohol.

Microwave heating/curing of silicone elastomers has many advantages over the conventional heating/curing. The most obvious ones are (1) heating and curing take place with substantially greater speed and uniformity and (2) the microwave can be turned on or off instantly minimizing wasted heat, i.e., energy conservation.

Experimental

Material. Polymer I was made by copolymerizing a mixture of octamethylcyclotetrasiloxane, $(Me_2SiO)_4$, and 2,4,6,-trimethyl-2,4,6-tris(3,3,3-trifluoropropyl)cyclotrisiloxane, $(MeCF_3CH_2CH_2SiO)_3$, in the presence of tetramethyldivinyldisiloxane, $ViMe_2SiOSiMe_2Vi$, using trifluoromethane sulfonic acid, CF_3SO_3H, as a catalyst. The polymerization procedure is described elsewhere (10).

Polymer II is a plant grade silicone polymer made by Dow Corning Corporation. The polymer was used without purification.

Polymer III was made by copolymerizing a mixture of octamethylcyclotetrasiloxane, $(Me_2SiO)_4$, and 2,4,6,8-tetramethyl-2,4,6,8-tetra-γ-mercaptopropyl-cyclotetrasiloxane in the presence of $Me_3SiOSiMe_3$ using trifluoromethane sulfonic acid, CF_3SO_3H, as a catalyst. The polymerization procedure is the same as that of Polymer I.

Copolymer IV and ethylene oxide containing copolymers were kindly provided by Mr. G. A. Vincent and Mr. W. D. Frank of Dow Corning Corporation respectively.

Microwave Heating/Curing. The microwave oven employed in this work has a frequency of 2450 $\bar{M}$ Hz. The material to be cured or heated was placed in a wide mouth glass jar. The jar was placed on the rotating base and the microwave (1 KW) was applied. After a given period of time (usually 5-10 min), the microwave was turned off and the sample was removed from the oven for examination. The author wishes to acknowledge Mr. F. C. Dall and Mr. R. J. Price of Dow Corning Corporation for their assistance.

Literature Cited

1. Zade, H.P., Heat Sealing and High-Frequency Welding of Plastics. Temple Press Limited, London, (1979), P. 79.
2. Kraiman, E.A., Encyclopedia of Polymer Science and Technology, (1966) 5, 1.
3. Hartshorn, L., Parry, J.V.L., and Rushton, E., Proc. Inst. Elect. Eng. (London) Part IIA, (1953) 100, 23
4. Von Hippel, A.R., Ed. Dielectric Materials and Applications, Tech. Press of M.I.T. and John Wiley & Sons Inc., New York (1954).
5. Vincent, G.A., Fearon, F.W.G., and Orbeck, T., 1972 Annual Report, Conference on Electrical Insulation and Dielectric Phenomena, National Academy of Science, P. 17.
6. Lee, C.L., U.S. Patent 4,011,197 (1977).
7. Homan, G.R., and Lee, C.L., U.S. Patent 4,039,504 (1977).
8. Homan, G.R., and Lee, C.L., U.S. Patent 4,066,603 (1978).
9. Kittle, R.E., and Ronk, G.M., U.S. Patent 4,026,844 (1977).
10. Lee, C.L., Marko, O.W., and Schulz, J.R., U.S. Patent 4,032,502 (1977).

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6

The Importance of Curing Conditions in Overall Energy Requirements for Organic Coatings

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Coatings for industrial finishing have been formulated over the years with only minor consideration given to the energy requirements for preparation, application, and curing. However, in recent years cost and availability of energy has become a very important consideration. Natural gas, which has been the common source of energy for curing coatings in convection ovens, has become short in supply necessitating industry shut downs for substantial time periods in some areas. (1-6)

Coil coating is one of the large segments of our industrial finishing industry. The coil coaters might more readily change to alternative methods for curing coatings than are open to other segments of the metals finishing industry. For example, coil coaters might change to induction heating or radiation curing (either infrared or electron beam) both of which use electricity as the energy source. The application of these methods to preformed metal objects, on the other hand, would be very difficult if not impossible because of the shapes of the objects. (4)

This paper examines the potential for energy savings offered to coil coaters by using electron curtain for curing instead of natural gas. It also examines the comparisons in cost for the two methods including comparisons of cost of the alternative coating materials.

Radiation Curing Coating Technology

Radiation curable coatings technology utilizes electrical energy and converts it either into light energy or an accelerated electron beam. The 100 percent reactive liquid coating systems associated with this technology absorb converted electrical energy from the processor unit (Light Source or Electron Accelerator) and undergo conversion to a solid matrix or cured finish. In the case of light-energy-convertible coatings a photoactive catalyst is required in order to initiate the curing mechanism. With electron beam the energy output is sufficient to cause direct ionization-radical formation and subsequent initiation curing reactions of the coating system.

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The majority of radiation curable materials are derived from or consist of acrylic and methacrylic unsaturated monomers, oligonomers, and polymers (including unsaturated polyethers) which cure through free radical addition-propagation reactions.

Energy Comparisons in Manufacture of Radiation Curing vs Conventional Coatings

Most of the radiation curable raw material technology is based on acrylic or methacrylic acid deritive but may also include modified epoxies, polyesters, and polyurethanes. Thus the backbones of radiation curing and conventional coatings are similar.

Conventional industrial coatings materials of the thermoset type are usually acrylic, polyester, epoxy, polyurethane or silicone resins dispersed or dissolved in organic or water/ether-alcohol coupling solvents. They are cured with gas convection or electric IR ovens. The raw materials for the polymers come from petroleum feedstocks which are processed or manufactured into a finished coating system.

Examples of some typical prepolymer materials and their raw material derivatives are given in Table I. Polymer manufacture schemes for radiation curable and conventional coatings are in Figures I and II. Qualitative comparison of a relative energy input intensity for preparation of radiation curable and conventional coatings are given in Tables II, III, and IV.

The point to be made is that most coating building blocks, conventional or radiation curable, come from approximately the same raw materials sources. The overall energy input for a manufacturing process involving conventional polymers is very similar or can be equivalent to manufacture of a radiation curable polymer system. In some cases there may be, however, an added processing step for the radiation curable polymer in order to include reactive functionality.

Radiation curable coating polymer systems are simple modifications of existing conventional solvent-based resin technologies. A solvent-based, standard hydroxyl-functional polyester resin can become a radiation curable resin through direct esterification of acrylic acid. Processing time (manufacturing) can be the same or slightly longer for radiation curable polymers but the only significant difference is attributed to acrylic acid content and increased raw material cost (RMC). Acrylic acid modification of 1000 grams of a hydroxyl functional linear polyester resin (1000 molecular weight) would result in approximately $0.10/lb price increase (RMC) based on acrylic acid cost of $0.40/lb (Cost comparisons are developed later).

In almost all cases a radiation curable polymer can be manufactured under the same conditions as conventional solvent based coatings except for special handling of possible toxic materials. Thus, differences in total energy requirements for both manufacturer and use (application and cure) are directly relatable to the energy consumed in application and curing.

In Energy Conservation in Textile and Polymer Processing; Vigo, T., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 1979.

TABLE I. RAW MATERIAL SOURCES FOR SELECTED CHEMICAL INTERMEDIATES USED IN THE COATINGS INDUSTRY

Compound Name and Formula	Sources of compound	Process	Total Production (Millons of Kilograms (lb) - year)
Acrylamide $CH_2CHCONH_2$ (C_3H_5NO)	Acrylonitrile, Conc sulfuric Acid, amonia or Sodium hydroxide	Hydration	18.2 (40)- 1973
ditto	Acrylonitrile water	Direct hydration over catalysts	See above
Acrylic acid C_2H_3COOH $(C_3H_4O_2)$	Ethylene oxide, Hydrogen cyanide, Sulfuric acid	Addition, Hydrolysis (Addition & Oxidation) (Process considered obsolete)	59.7 (131.6)- 1973 431 (948.)- 1974 (includes esters)
ditto	Propylene-air	Oxidation	See above
	---		614.8 (1354.2)-
Acrylonitrile CH_2CHCN	Ethylene cyanohydrin	---	1973; 642 (1412)-
(C_3H_3N)	Acetylene, HCN	---	1974 552 (1215)- 1975
Adipic acid $COOH(CH_2)_4COOH$ $(C_6H_{10}O_4)$	Cyclohexane air, catalyst nitric acid	Oxidation	711 (1567)- 1973 764 (1630)- 1974 668 (1470) 1975

In Energy Conservation in Textile and Polymer Processing; Vigo, T., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 1979.

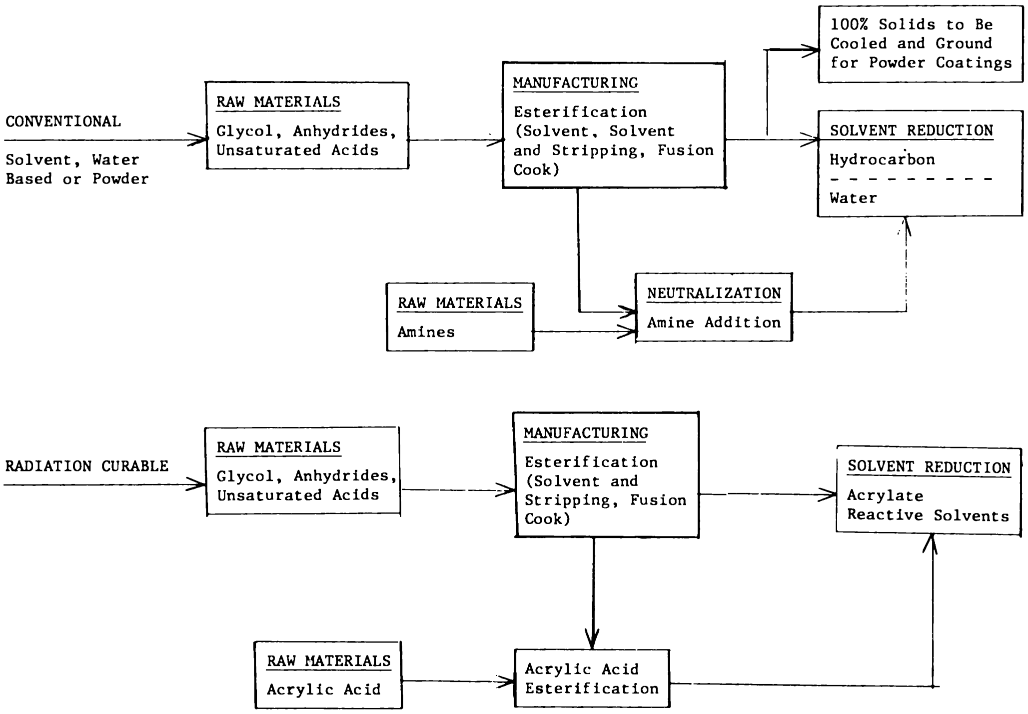

Figure 1. Polyester manufacture

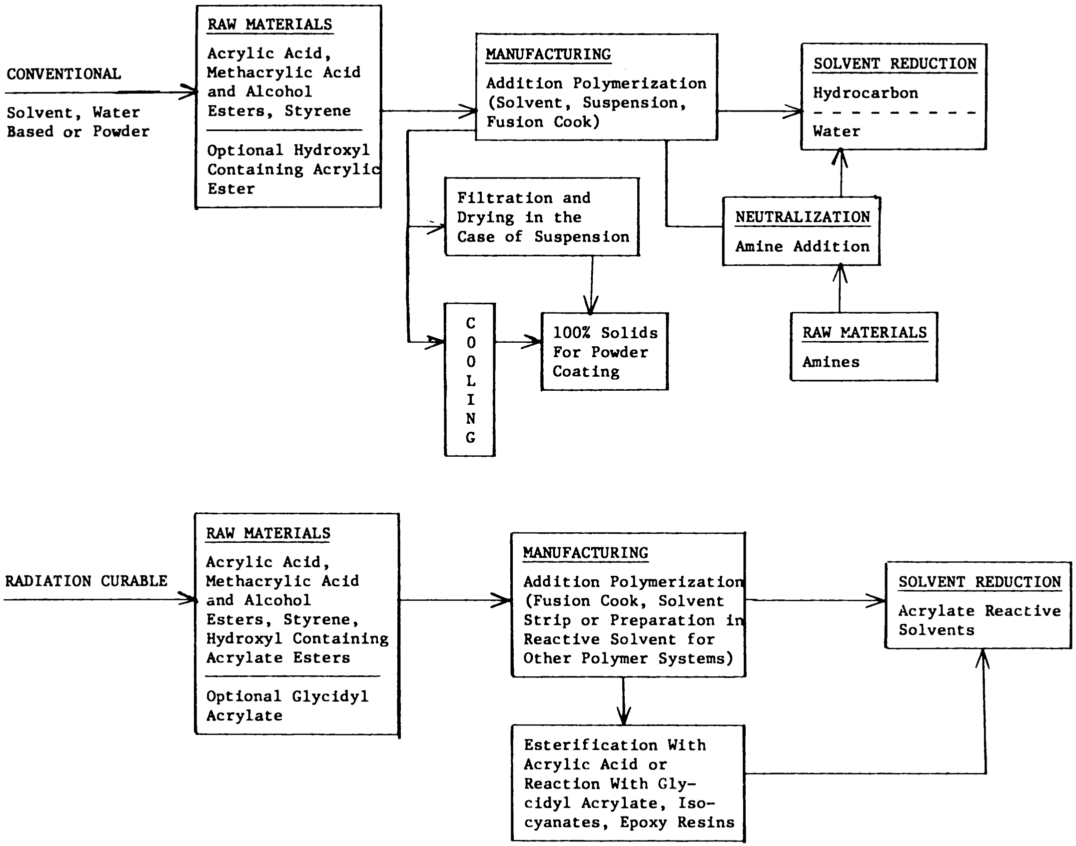

Figure 2. Acrylic manufacture

TABLE II. ENERGY INPUT FOR POLYESTER MANUFACTURE

Technology	Raw Materials	Manufacturing Procedure	Temperature Requirements in Manufacture	Relating Energy and Raw Material Cost (RMC) Input for New Technology Versus Standard
Conventional solvent-based systems 30-80% solids	Acid, Anhydrides 0.28 — 0.50/lb glycols alcohols 0.25-0.50/lb	1 day Fusion cook (8-16 hr) or 1 day Solvent cook	(A) 200-300°C (B) 100-200°C	(A) High energy input (B) Low energy input
Powder 100% solids	Same as conventional	1 day Fusion cook and 1/2 day cooling/grinding	200-300°C 0°to room temp.	RMC equal but process is slightly greater than high energy input standard (A) and much greater than (B)
Water 30-60% solids	Same as conventional + amine and coupling solvent costs amine = 0.40/lb solvent = 0.35/lb	1 day solvent cook and 1/2-1 day neutralization	100-200°C 30-100°C	RMC for water-based systems are greater as well as processing time
Radiation curable 100% reactive	Same as conventional + acrylic acid = 0.40/lb	1 day Fusion cook followed by reactive solvent addition and low-temperature esterification 1/2 day	200-300°C less than 130°C	Same as (A) but added second reaction step + cost of acrylic acid
Radiation curable 100% reactive	anhydride + propylene oxide addition + acrylic acid	1 day solvent cook and esterification	100-200°C	Equal to low energy standard (B) except for added cost of acrylic acid

TABLE III. ENERGY INPUT FOR ACRYLIC RESIN MANUFACTURE

Technology	Raw Materials	Manufacturing Procedure	Energy Intensity For Manufacture	Relative Energy and Raw Material Cost (RMC) Input for New Technology Versus Standard
Conventional Solvent-Based Systems 30-60% Solids	Acrylic monomers acrylic acid 0.30-0.80/lb	Fusion cook 1 day	(A) 200-300°C	(A) High energy
		1 day solvent cook	(B) 80-200°C	(B) Low Energy
Powder 100% solids	Same as contional	Fusion cook 1 day + 1/2 day cooling/ grinding	200-300°C	RMC are equal to the standard (A) but processing is slightly more energy intensive
		Suspension polymers 1 day + 1/2 day filtration/drying (1 day)	80-100°C	RMC is equal but processing time is much greater than standard system (B)
Water 30-60% solids	Same as conventional + amines and coupling solvents 0.30-0.60/lb	1 day solvent cook and 1/2 to 1 day neutralization--let-down	80-200°C 30-100°C	RMC for water-based system are greater as well as increase in processing times
Radiation curable 100% reactive	Same as conventional + acrylic acid or glycidyl acrylate 0.40 ≃ $2.00/lb	Fusion cook 1 day followed by reactive solvent reduction and subsequent acrylic acid esterification (1/2 day)	200-300°C less than 130°C	Same as (A) but added second reaction step + cost of acrylic acid

TABLE IV. COATINGS FORMULATION COMPARISONS

	Solvents	Crosslinking Resins	Polymers	Formulation
Conventional Solvent-Based Coatings	Aliphatic- Aromatic Hydrocarbons	Melamine Epoxy Blocked isocyanates	Polyester Acrylic Epoxy Urethane	40-60% solvent 30-40% polymer 10-20% crosslinking resin
Water-Based Coatings	Water Alcohols/ether cosolvents amines	same as conventional	same as conventional	10-20% crosslinking resin 10-20% cosolvent
Powder	----	Melamine epoxy blocked isocyanate	Polyester acrylic epoxy	10-20% crosslinking resin
Radiation Curable	Reactive acrylates-vinyl 2EHA, NVP, etc	Multifunctional di or triacrylates	same as conventional but are usually substituted with acrylic-methacrylic acids	10-30% multifunctional acrylate 10-50% polymer 20-50% reactive solvent

Potential Energy Savings By Using Electron Curing of Coatings on a Coil Coating Line

The following sections are based upon recent analysis(7) (8) of the energy requirements using electron curing vs conventional curing on a 60-inch wide line on which coated aluminum strip is running at 300-feet per minute. It is assumed that one mil of dry film is needed for the finished product -- no consideration of the primer coat is included in these analyses. Three types of topcoats are considered which would be typical of those being used with thermal curing for either aluminum or steel coil. The first considered is a 45% solids conventional solvent paint; the second is a 45% solids water based system, while the third is a 45% solids coating which has 80% water and 20% solvent. All of these coatings cure at a metal temperature of 425 F and dwell time of 30 seconds. The ovens considered are convective with natural gas or electricity used to heat the units, and an oven temperature of 600 F is assumed. The solvent systems utilize an afterburner for pollution control, which is gas fired. Cases for preheat and no preheat of the oven exhaust air are considered.

Based on the assumption of a 30 second dwell time, an oven length of 150 feet is indicated. An oven 6 feet wide by 2 feet deep is assumed with end openings of 0.5 feet by 6 feet. The total surface area of the oven is 2570 square feet. The end openings are 6 square feet in area. Based upon heat loss figures of 0.3 BTU/ft^2/hr and 54 BTU/ft^2/hr respectively for the oven surface and its end openings, the respective heat loss figures for the oven are 409,000 and 172,000 BTU/hr for an ambient temperature of 70 F.

The weight of the metal coil processed will be based upon a rolled thickness of 0.0254 inches, with coil 5 feet wide moving at 300 feet per minute. Since aluminum has a density of (2.70 g/cc) 169 lb/ft^3, the sheet weighs 0.357 lb/ft^2. Since 90,000 ft^2 of coil are processed per hour, a throughput weight of 32,130 lb/hr results.

The heat energy required to elevate this mass of coil to the cure temperature of 425 F from the ambient 70 F can be readily calculated, based upon the specific heat for aluminum of 0.215 BTU/lb/F. This heat input figure is found to be 2.45 x 10^6 BTU/hr.

Finally, the energy required to evaporate one pound of water from the coating at 70 F to vapor at 600 F is found to be 1296 BTU/lb. These basic parameters/relations for the curing system can now be used in analyzing the energy requirement of the curing oven.

Conventional Solvent Paint. Based upon a solvent paint of 45% solids content, the 1.0 mil dry film thickness will require a 2.22 mil wet film thickness and a solvent content of 68.4 gallons per hour for a 90,000 ft^2/hr throughput. If one takes an exhaust ratio of 166 ft^3 of air per minute, per gallon of solvent per hour removed, the air exhaust requirements for the oven are 11,350 ft^3/minute at 70 F. The energy required to heat this air to 600 F from the ambinet temperature, is found to be 6.5 x 10^6 BTU/hr.

The <u>total</u> heat energy input Q_0 to the oven is therefore made up of the thermal content of the metal, the oven panel loss, the oven sillouette opening loss and the exhaust air loss

$$\begin{aligned} Q_0 &= (2.45 + 0.41 + 0.17 + 6.5) \times 10^6 \text{ BTU/hr.} \\ &= 9.5 \times 10^6 \text{ BTU/hr.} \end{aligned}$$

The calculations for oven air exhaust requirements are as follows: The exhaust requirement

$$= \frac{10{,}000 \text{ ft}^3 \text{ of air at 70 F (SCF)}}{\text{gallon of solvent}} \quad \frac{\times\ 68.4 \text{ gallon}}{60 \text{ minutes}}$$

$V_{70\ F}$ = exhaust at 70 F reference, i.e., 11,350 ft^3/ minute Since air expands when heated, an adjustment is required to insure for correct quantities of 70 F air entering the oven. This correction factor (adjusted exhaust rate on actual fan capacity at oven temperature) can be found for the following relationship:

$$V \text{ oven temperature} = \frac{460 \text{ F} + \text{oven temperature}}{530 \text{ F}} (V_{70\ F})$$

Then for $V_{70\ F}$ = 11,350 SCFM and oven temperature = 600 F
V oven temperature = 22,750 or approximately 23,000 CFM

The power requirements of the fans are estimated to be 20 hp for the circulation volume of 26,000 cfm, and 15 hp for the exhaust blower volume of 23,000 cfm at 600 F oven temperature. Hence, the fan power requirements Q_f are 35 hp or 26.1 kW.

Some estimates of the afterburner energy requirements Q_A are included in the Appendix. The net heat input for the afterburner with a single zone preheat is found to be 0.81 x 10^6 BTU/hr. With no preheat, the estimated requirement is 5.8 x 10^6 BTU/hr.

Some estimate of the natural gas requirements can now be made, based upon an assumed yield of 1000 BTU/cu ft and 10,500 BTU/kWhr. Therefore, the gross energy input per hour, with single zone preheat will be:

$$\begin{aligned} Q_{tot} &= Q_0 + Q_f + Q_A \\ &= (9.5 \times 10^6) + (26.1 \times 10{,}500) + (0.81 \times 10^6) \\ &= (9.5 + 0.3 + (0.8)\ 10^6 \\ &= 10.6 \times 10^6 \text{ BTU/hr.} \end{aligned}$$

At a gas cost of \$2.50 per 1000 ft^3, and power costs of 3¢/kWhr, the hourly energy cost of the system for the solvent paint will be:

$$\begin{aligned} C_{tot} = C_{gas} + C_{elec} &= (10.3 \times \$2.50) + (26.1 \times 0.03) \\ &= 25.75 + \$0.78 = \$26.53 \end{aligned}$$

If no afterburner preheat is employed, these numbers become:

$C_{tot} = 15.6 \times 10^6$ BTU/hr at an hourly operating energy cost of

$$C_{tot} = \$38.25 + \$0.78$$
$$= \$39.03$$

One can readily calculate the cost to operate the same oven with electricity. Using the rough figure of 1000 kWh ≈ 3 MBTU, we see that a power consumption of from 3-5000 kWhr is indicated. Even at the relatively liberal electrical power cost of 3¢ per kWh, the hourly operating cost would be at least three times as high. This would be expected on <u>equivalent</u> net energy cost figures, as the 10,500 BTU figure for 1 kWh is based upon a 33% conversion efficiency at the electrical power station.

<u>Water Base Paint - No Solvent</u>. As in the case above, the 45% solids water based system will present a removal burden of 68.4 gallons to the oven. This represents 570 pounds/hour which must be removed, or a heat input of 0.74×10^6 BTU/hr for evaporation.

The exhaust volume required to provide a dry oven environment at this level of water removal, will be 5700 cubic feet-/hour of air at 70 F, or a thermal input of 3.26×10^6 BTU/hr to elevate this 5700 cubic feet of air to a temperature of 600 F (see Appendix).

As in the section above, the oven input will be made up of the energy investment in the metal, the oven panel loss, the opening loss, the exhaust air loss and the heat input to evaporate the water:

$$Q_0 = (2.45 + 0.41 + 0.17 + 3.26 + 0.74)\ 10^6 \text{ BTU/hr}$$
$$= 7.03 \times 10^6 \text{ BTU/hr}$$

The power requirements of the fans are estimated to be 30 hp for the circulation volume of 42,600 cfm, and 10 hp for the exhaust of 11,400 cfm. Hence, the fan power requirements Q_f are 40 hp or 29.8 kW.

As before, the gross energy input per hour for the water based system can be estimated:

$$Q_{tot} = Q_0 + Q_f$$
$$= 7.03 \times 10^6 + (29.8 \times 10{,}500)$$
$$= (7.03 + 0.31)\ 10^6$$
$$= 7.34 \times 10^6 \text{ BTU/hr}$$

At a gas cost of \$2.50 per 1000 ft³ and power costs of 3¢/kWhr one arrives at an hourly energy cost of the system for water based paint of:

$$C_{tot} = C_{gas} + C_{elec}$$
$$= (7.03 \times \$2.50) + (29.8 \times .03)$$
$$= 17.58 + 0.89$$
$$= \$18.47$$

The Water Base Paint in an 80/20 Blend. In this case, a 45% solids coating will be utilized with an 80% water and 20% solvent base. As before, 68.4 gallons of water and solvent will be removed per hour of operation for a total of 456 pounds of water. This, in turn, will require a heat input of 0.59 x 10^6 BTU/hr for evaporation.

The exhaust rate required to provide a safe and dry oven atmosphere can then be determined for each component of the coating. If, as in the first case, one utilizes a figure of 166 cfm per gallon of solvent/hr removed, the 13.7 gallons of solvent per hour requires: 2271 of cfm of 70 F air.

If one assumes a figure of 10 cfm/lb of water/hr, the 456 lbs of water requires: 4558 cfm of 70 F air.

The energy required to heat the replacement air to the 600 F required at this rate (6829 cfm), from a 70 F ambient temperature, can be calculated to be 3.91 x 16^6 BTU/hr.

As before, the oven input will then be made of the energy investment in the metal, the oven panel loss, the opening loss, the exhaust air loss and the energy required to evaporate the water:

$$\begin{aligned} Q_0 &= (2.45 + 0.41 + 0.17 + 3.91 + 0.59)\ 10^6 \text{ BTU/hr} \\ &= 7.53 \times 10^6 \text{ BTU/hr} \end{aligned}$$

The power requirements for the fans are estimated to be identical to that of case 3 or 29.8 kW (Appendix)

As before, the gross energy input per hour for the 80/20 system can be estimated as:

$$\begin{aligned} Q_{tot} &= Q_0 + Q_F \\ &= (7.53 \times 10^6) + (0.3) \times 10^6) \\ &= 7.84 \times 10^6 \text{ BTU/hr} \end{aligned}$$

At a gas cost of \$2.50 per 1000 ft^3 and power costs of 3¢/kWhr, one arrives at an hourly energy cost for the 80/20 system of:

$$\begin{aligned} C_{tot} &= C_{gas} + C_{elec} \\ &= (7.53 \times \$2.50) + (29.8 \times .03) \\ &= 18.82 + 0.89 \\ &= \$19.71 \end{aligned}$$

Electron Curing of a 100% Solid System. In order to assess the comparative merits of an electron curing system, it is first necessary to specify the energy investment to cure (or dose to cure) requirements of the coatings. At the present time, the electron curable 100% solids systems suitable for interior metal decorating applications possess cure doses in the range of 2.5 megarads (6 cal/gm or 26 BTU/lb). (2) It is likely that radiation curable coatings with exterior durability will soon become available with energy investments to cure not much in excess of this figure.

Under these conditions, a single curing station at an electron beam power output of approximately 300 watts per inch is adequate to cure such a coating at a line speed of 300 feet/minute. For the application treated here, a 175 kV x 155 cm unit operating at a beam current of 100 MA would suffice -this is the CB 175/155/100 unit - it provides a beam output of 17.5 kW at an input power of 21.5 kilowatts.

The coatings currently available for electron curing are free radical initiated addition polymerized systems - utilizing unsaturated oligomers and acrylic momomers. Since these reactions are oxygen inhibited, inerting of the process zone is usually required, although non-acrylic coatings chemistry is now well developed which shows near term promise of non O_2 inhibited systems. In order to present a realistic comparative analysis, the cost of inert gas should be included. Current inerting systems in commercial practice are based upon inert gas generators which (simply) provide a dried, compressed source of the products of combustion. The fuel source for these generators is typically natural gas or fuel oil. The former will be considered here since it is the most pertinent to the present analysis.

For a 5 foot line running at 300 feet per minute, an inert gas supply of ∼50 cfm or 3000 cfh will be required using the present coating systems (which will cure well in a few thousand ppm of O_2). Such a generator will require 12% of this output in natural gas, or ∼400 cfh to fire it. Some of the important operating parameters for such an inert gas system (5) (Selas SGV 100) are as follows:

Output Volume: 3540 cfh or 100 m^3/hr

Gas (Methane): 414 cfh or 11.7 m^3/hr

Cooling Water: 1980 gph or 7.5 m^3/hr

Power*: 20 kW

*Includes 15 hp compressor for providing ouput at 100 psi.

The total energy requirements for this system will be made of the input to the electron processor, the fuel for the inert gas system and its compressor power:

$$\begin{aligned} Q_{tot} &= Q_{eb} + Q_{ig} \\ &= (21.5 \times 10{,}500) + (414 \times 1000) + (20 \times 10{,}500) \\ &= 0.23 + 0.41 + 0.21 \\ &= 0.85 \times 10^6 \text{ BTU/hr} \end{aligned}$$

At a gas cost of \$2.50/1000 ft^3 and power costs of 3¢/kWhr, one arrives at an hourly energy cost for the 100% solids curing system of:

$$\begin{aligned} c_{tot} &= C_{gas} + C_{elec} \\ &= (0.41 \times \$2.50) + (41.5 \times .03) \\ &= 1.03 + 1.24 \\ &= \$2.27 \end{aligned}$$

In a comparative cost analysis of the electron vs. thermal curing stystems, a maintenance cost should be assigned to each system. In the case of the eb unit, it is about one dollar per hour; for thermal ovens of this size, it is of the same order. Water costs for the inert gas generator are not included, but would add about 40¢/hr.

A summary of these comparative energetics is tabulated below

Method	Coating	Afterburner	Total Energy* (10^6 BTU/hr)	Total Gas (1000cfh)	Cost ($/hr)
Thermal	Solvent	No Preheat	15.7	15.4	40.03
		Preheat	10.7	10.4	26.78
Thermal	Water		7.3	7.0	18.47
Thermal	80/20		7.8	7.5	19.71
Electron	100% Solids		0.85	.4	2.27

* Using 1 kWhr = 10,500 BTU for electrical power: thermal energy conversion.

Comparisons in Cost of Electron Curing Coatings Materials vs Conventional Coatings

The cost of radiation curable coatings in large volume can be equivalent to, or slightly more expensive than conventional coatings depending on the polymer desired, the cost of the starting materials and added manufacturing processes. This conclusion is based on hypothetical comparison's of costs as discussed below.

A sample calculation for raw material costs (RMC) of a conventional polyester resin synthesis is shown below.

5 moles of phthalic anhydride = (5 moles) (148.12 g/mole)
= 740.6 g
740.6 g/454 g/lb = (1.63 lb) ($0.26/lb) = $0.42
6 moles of ethylene glycol = (6 moles) (62.07 g/mole)
= 372.42 g
372.42 g/454 g/lb = (0.082 lb) ($0.25/lb) = $0.21
Molecular wight of the polyester resin = (5 moles phthalic anhydride) + (6 moles ethylene glycol) - (5 moles of H_2O).
740.6 + 372.42 - (5) (18) = 1023.02 gms/mole
Total lb of polyester resin made = 2.45 lb
Minus water of reaction - 0.20 lb
2.25 lb
Total cost = $0.63 for 2.25 lb material = $0.63/2.26 lb = $0.28/lb

The above calculations are based on a theoretical molecular weight of 1000 with prices of bulk monomer quantities taken from CMR, February 27, 1978, resulting in a total material cost for the final product of $0.28/lb. (RMC phthalic anhydride, $0.26/lb; RMC ethylene glycol, $0.25/lb). Manufacture is by simple fusion cook or solvent azeotropic water removal.

Similar calculations are shown below for a radiation curable polyester but included is the cost of acrylic acid (0.37/lb) and an extra manufacturing cost step (0.10/lb) for the acrylic acid-polymer esterification.

5 moles of phthalic anhydride = (1.63 lb) ($0.26/lb) = $0.42
6 miles of ethylene glycol = (0.82 lb) ($0.25/lb) = $0.21
2 moles of acrylic acid = (0.32 lb) ($0.37/lb) = $0.12
Molecular weight of the polyester resin = (5 moles phthalic anhydride) + (6 moles ethylene glycol) + (2 moles acrylic acid) - (7 moles of H_2O) = 987.
Total lb of acrylated polyester resin made = 2.17 lb.
Total cost = $0.75 for 2.17 lb.
$0.75/2.17 lb = $0.34/lb.
Added manufacturing cost for acrylic acid reaction $0.10/lb.
Total cost of radiation curable resin = $0.44/lb.

The total RMC plus extra manufacturing cost for the polymer (radiation curable) is $0.44/lb. This is approximately $0.16/lb more in cost for the same molecular weight polymer as used in conventional coating systems.

The individual RMC for polymer materials is not the only factor in cost analysis of a coating system. In order to make a fair comparison between conventional and radiation curable coatings one must consider the entire coatings formulation. Shown below is a cost range calculated for a conventional solvent-containing resin (excluding pigmentation) using the $0.28/lb polyester resin cost calculated earlier.

Low Solvent Range	%	Cost/lb($)		Cost($)
30% polyester resin	(0.30)	(0.28)	=	0.08
50% solvent	(0.50)	(0.06)	=	0.03
20% melamine resin	(0.20)	(1.00)	=	0.20
				0.31/lb
High Solvent Cost Range				
30% polyester resin	(0.30)	(0.28)	=	0.08
50% solvent	(0.50)	(0.55)	=	0.28
20% melamine resin	(0.20)	(1.00)	=	0.20
				0.56/lb

Low range = ($0.31/lb cost) (9 lb/gal) = $2.79/gal
High range = ($0.56/lb cost) (9 lb/gal) = $5.04/gal.
These coatings formulations are 50% solids and their coatings coverage is only 650 to 800 ft^2/gallon.

For comparison, the cost of a comparable radiation curing coating is shown below:

	%	Cost/lb($)		Cost($)
30% acrylated polyester resin	(0.30)	(0.44)	=	0.13
50% 2-ethyl hexyl acrylate	(0.50)	(0.44)	=	0.22
20% multifunctional acrylate	(0.20)	(1.10)	=	0.22
				0.57/lb

The cost of the radiation curable coatings formulation is $5.13/gal ($0.57/lb x 9 lb/gal = $5.3/gal: at 100 percent solids). This cost/gallon is comparable to the high range solvent-based system, but the coverage is now 1600 to 1625 ft^2.

In direct comparison to the conventional systems, radiation curable coatings formulations can be constructed with lower cost than conventional solvent systems on a square foot of coverage basis. It takes $2.79 to $5.04 of coatings material (this is range in cost per gallon of material) of solvent-based conventional coatings to cover 650 to 800 ft^2. Since coverage of the radiation curable coating system is 2 to 2.5 times greater than the 50% solids coatings, the actual cost for equal coverage of the radiation curable material is $5.13/gal ÷2 or 2.5, resulting in $2.05/gal to $2.56/gal for equal coverage.

This savings amounts to about $0.23 to $0.74/gal in the low solvent range, and about $3.00/gal in the high solvent cost range.

Comparisons in Cost of Equipment Amortization for Radiation Curing vs. Conventional Coil Coatings

The aforementioned model of a coil coating line provides for a cost analysis of electron curing compared to conventional curing of coatings on a coil coating line.

For this analysis certain assumptions have been made.

(1) Two shifts, 5 day/week operation
(2) Coating capacity - 12,000 ft^2/day
(3) Coating thickness - 0.001 inch on 0.020 inch steel
(4) Capital expenditures under a mortgage at 15% for 10 years making annual payments of 20% of initial cost for each of the first 10 years
(5) Cost of floor space - $10/$ft^2$.

If a gas-fired oven costs $200,000, and an incinerator for emission control costs $75,000, this results in an hourly cost of:
($200,000) (0.20/yr) (10 years) ÷ (10 years) (50 weeks/yr) (5 days/wk) (16 hr/day) = $10/hr
($75,000) (0.20) (10) ÷ $40,000 = $3.75/hr
An Electrocure radiation curing unit could cost up to $400,000 or a capital expenditure cost of $20/hr. Radiation curable systems also require more maintenance and an inert atmosphere (nitrogen blanket) to ensure efficient curing operations.

Summary of Cost Comparisons for Radiation-Cured vs. Conventional Coatings on a Coil Coating Line

The previous sections have shown that considerable energy savings can be accomplished by substituting radiation curing for conventional ovens in a coil coating line.

The coil coatings management today is certainly interested in saving energy, but its major concern is the cost of the coating, assuming equal performance for the finished product. Thus it is important to examine carefully the overall costs of coil coatings when cured by radiation and natural gas. These costs are tabulated below:

	Cost Breakdown ($/hr) of Solvent-Based Conventional Coating System	Cost Breakdown ($/hr) of Radiation (Electron Curtain) Cured Coating System
Cure Equipment	10.00	20.00
Aux. Equipment	3.75	--
Natural Gas	10.50	---
Electricity	0.35	0.70
System Space	0.75	0.03
Storage Space	0.50	---
Labor	15.00	10.00
Coating Cost	51.62 to 93.24/650 to 800 ft^2	37.96 to 47.45/650 to 800 ft^2
Maintenance	0.50	1.50
Nitrogen	---	1.20
Total Operating Cost	$92.97 to $134.59/hr.	$71.39 to $80.88/hr.

The coatings material cost calculations shown above were developed earlier for an idealized coil coating operation. The method of coil coatings operational calculations were taken from References 7, 8, 9 and 10 and applied to the present coatings cost comparisons. Coatings consumption is 18.5 gal/hr and solvent-based coatings average cost range is $2.79 to $5.04/gal, giving a total cost of $51.62 to $93.24/hr.

The cost of the radiation curable coatings formulation is $5.13/gal, but it covers 2 to 2.5 times more surface area than the solvent-based coating. The cost for equal coverage of radiation curable coating is $18.50 gal/hr ÷ 2 or 2.5 times $5.13/gal = $37.96/hr to $47.45/hr.

Thus, under ideal conditions, radiation curable coatings might be formulated or designed to show a lower or equal cost per square foot of coverage when compared with solvent-based coatings without even considering energy and space savings calculations.

In all of these calculations there has been no added value (profit, research dollar spending, etc.), attached to the figures. These calculations are idealized and try to reflect possible raw materials cost at the present time.

It is theoretically possible at the present time to formulate (radiation cured) coatings systems with almost equivalent RMC (raw materials cost) at equal coverage as conventional systems. As the use of RC systems becomes more widespread the cost for expensive reactive monomer, prepolymer components should also drop. This would occur as large scale efficient manufacturing processes are adopted to handle larger volumes. This lowering of price for RMC of the individual RC coatings components as well as energy and space savings will also be attractive to end users.

One of the major disadvantages of RC versus conventional coatings, at the present time, is the final coatings properties obtained under a given set of cure. This is especially true in coil coatings operations where the required performance charac-

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teristics are extreme and difficult to obtain, and the substrate/coating throughput is very fast. Much more research is still needed on RC systems in order to match diverse coil coating product lines and complex coating performance characteristics.

Appendix

Estimates of the Heat Input for the Operation of the Afterburner for the Conventional Solvent Paint. Based upon the calculated exhaust rate of 11,350 cfm of 70 F air, one can estimate the required hourly heat input Q from the relation: Q =

$$Q = mc\Delta t$$

where m is the mass of air moved per hour, c its specific heat and Δt the temperature change. For the case of the afterburner, a 1400 F burner temperature is assumed. The theoretical input is

$$Q_t = 9.99 \times 10^6 \text{ BTU/hr}$$

Since the incineration process is only 75% efficient,

$$Q_a = 13.32 \times 10^6 \text{ BTU/hr}$$

Now the solvent (e.g., cyclohexanone) will yield 14,000 BTUs/lb upon incineration, so that the 68.4 gallons of solvent burnt per hour have a thermal yield of

$$Q_s = 7.52 \times 10^6 \text{ BTU/hr}$$

The net heat input to the afterburner

$$\begin{aligned} Q_n &= Q_a - Q_s \\ &= 5.81 \times 10^6 \text{ BTU/hr} \end{aligned}$$

In order to increase the afterburner efficiency, a single preheat zone elevates the input air from 600 F to 900 F. For this condition:

$$Q^1{}_t = 6.24 \times 10^6 \text{ BTU/hr}$$

$$Q^1{}_a = 8.33 \times 10_6 \text{ BTU/hr}$$

And the net input to the afterburner with a single preheat zone is now reduced to:

$$\begin{aligned} Q^1{}_n &= Q_a - Q_s \\ &= 0.81 \times 10^6 \text{ BTU/hr} \end{aligned}$$

Estimate of the Heat Input for the Exhaust Air for Water Base Paint With No Solvent. The air exhaust rate required to provide a dry oven atmosphere is determined by the amount of water released into the oven. Using a figure of 10 cfm of air per pound of water per hour, the 570 pounds of water per hour will require approximately 5700 cfm of air at 70 F.

As in the example above, the hourly heat input required to heat this amount of air is:

$$Q = mc\Delta t$$

where $m = (5700 \times 60)$ cfh $\times$ (0.075 pounds/ft^3)

$c = 0.24$ BTU per lb per F

$t = 600 - 70 = 530$ F

So the heat input

$$Q = (34.2 \times 10^4)\ (0.018)\ (530)$$
$$= 3.26 \times 10^6 \text{ BTU/hr}$$

Estimation of the Circulation Fan Power for the Water Base Paint. Consider first the heat input required for the metal, the water removal, the end losses and the oven panel losses. Call this Q_1, made up of:

$$Q_1 = (2.45 + 0.74 + 0.41 + 0.17)\ 10^6 \text{ BTU/hr}$$
$$= 3.77 \times 10^6 \text{ BTU/hr}$$

We can now calculate the air volume V_1 in cfm required to provide this input at 70 F from

$$Q_1 = V_1\ \Delta t\ 60\ \rho c \text{ so } V_1 = Q_1/(60\ \Delta t\ \rho\ c)$$

where ρ is the air density in lb/ft^3, and c its specific heat and Δt the operating head temperature differential of 200 F.

$$V_1 = 3.77 \times 10^6/2.16$$
$$= 1.74 \times 10^4 \text{ cfm at 70 F}$$

Secondly, the additional heat input per hour for the exhaust air, $Q_2 = 3.26 \times 10^6$ BTU/hr. In the same manner, one can calculate the total heat for its delivery from:

$$\Delta t = Q_2/(60\ V_1\ \rho c)$$
$$= (3.26 \times 10^6)/(60 \times 1.74 \times 10^4 \times 0.018)$$
$$= 173 \text{ F}$$

Operating head (200 F) + oven temperature (600 F) = delivery temperature (800 F) and delivery temperature - total head = mixed temperature.

Hence 800 F - 173 F = 627 F

The circulating volume at 70 F, hence the capacity of the circulating fan at that temperature, is V_1 corrected to the mixed temperature of 627 F, or

$$2.05\ V_1 = 2.05 \times 1.74 \times 10^4$$
$$= 35{,}800 \text{ cfm}$$

The exhaust volume, calculated to be 5700 cfm at 70 F, will provide the exhaust blower requirement of 600 F air, or 2.00 x 5700 = 11,400 cfm.

In order to achieve a circulating volume of 35,800 cfm at a static pressure of 2.5 inches, 2 x 21,000 cfm fans with 15 hp motors are needed. Their power consumption is therfore 22.4 kilowatts.

In order to achieve an exhaust volume of 11,400 cfm at a static pressure of 2.5 inches, an 11,700 cfm blower with a 10 hp drive motor is required. Its power consumption is therefore 7.46 kilowatts.

Acknowledgement

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Literature Cited

1. Editorial, "Paint Curing: Saving 27.8 Billion BTUs/Year". Products Finishing, March 1977, pp 77-79.
2. David, Mary P., "Energy Consumption Outlook for the Printing Industry". Inland Printer/American Lithographer, February 1977, p. 60.
3. Toronto and Montreal Societies for Coatings Technology, Joint Symposium, Sept. 14, 1977. "Energy Conservation in Paint Production". American Paint and Coatings Journal, August 15, 1977, p. 9.
4. Anderson, R. J., "The Energy Reason for Using Coated Coil". Metal Finishing, November 1977, pp. 20-22.
5. Dekoker, Neil, "Energy Conservation in Manufacturing". Industrial Engineering, December 1977, pp. 20-26.
6. Evaluation of the Theoretical Potential for Energy Conservation in Seven Basic Industries. Battelle Columbus Laboratories Report to FEA, January 31, 1975.
7. Powers, H. R., "Electron Beam Curing for Coil Coatings, A Study of The Energy Requirements". Sherwin-Williams Company, 1975.
8. Powers, H. R., "Comparison of Energy Requirements for Various Methods of Curing Coil Coatings". Sherwin-Williams Company, 1973.
9. Rothchild, R. D., Painting Highlights, Nov./Dec., 1977, p. 16.
10. Product Data Sheets of following companies: Electron Beam Curable Coatings of Interior and Exterior Durability, Sherwin Williams Co., Chicago, Il., 1977; UCARV-280 and 281, Radiation Curable Coatings for Metal Decoration, Union Carbide Corporation, 270 Park Ave., New York, 1976; Reactomer Monomers for Radiation Cured Coatings, Thiokol Chemical Div., Thiokol Corp., Trenton, N. J., 1976; Coatings for Aluminum Coil Mobil Chemical Co., Edison, N. J.

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Electron-Curable Coatings and Adhesives: Formulation Basics and Application Technology

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A. Formulation Basics

1. Introduction. Industry-wide concern over natural gas consumption in thermal curing processes and solvent emissions from conventional formulations has generated increasing interest in the use of solvent-free radiation curable coatings and adhesives. In spite of these strong driving forces for the development of such compositions, industrial adoption of radiation curing is growing at a very slow rate at present. Some of the key reasons for this slow growth can be more clearly understood by considering the criteria which must be met by an acceptable radiation curable formulation. These include:

a) Efficient conversion at useful line speeds.
b) Safety in handling in an industrial environment.
c) Smooth application at desired coating weight.
d) Acceptable overall economics.
e) The necessary physical properties in a final product.

Simultaneous satisfaction of all of these requirements limits the number of materials which can be used in formulations. The relationships between formulation materials and the above criteria provide the basis for practical radiation curable products.

2. Radiation Curable Materials. The exposure of a material to electron beam (EB) radiation produces free radicals randomly by bond breaking. If components are chosen which are capable of undergoing a free radical initiated polymerization, the composition can be rapidly converted from a liquid to a solid polymer film. Although some monofunctional monomers can be converted fairly efficiently to polymeric material using EB radiation, the products are generally soft films with poor integrity. On the other hand, multifunctional materials, such as di- or trifunctional monomers or resinous materials, will generally be converted to a hard, brittle film, with poor adhesion and flexibility. These multifunctional materials generally provide an excessive

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amount of crosslinking when fully cured and monofunctional monomers are required in order to reduce this crosslinking. Such mixtures of mono- and multifunctional materials can provide a wide range of physical properties when properly balanced.

Of the many types of polymerizable materials which have been studied, acrylic functional materials have generally been found to provide the fastest cure rates by EB radiation, particularly when exposed in an atmosphere with a lowered oxygen content. The present discussions will generally refer to such acrylate-functional materials cured in an inert atmosphere.

A typical EB curable formulation will generally consist of a relatively high molecular weight solid or semi-solid difunctional acrylic resin reduced to application viscosity with combinations of liquid mono- and multifunctional acrylic monomers. These acrylic monomers, along with a few other selected polymerizable monomers, serve as reactive diluents and allow formulation of solvent-free compositions. Usually, small amounts of additives are also used in order to provide special properties, such as slip.

The selection of liquid monofunctional monomers for use in EB cure has been a key factor in the slow pace of development of acceptable formulations. These monomers play dominant roles in determining cure speed, viscosity, safety and cost, in addition to significant contributions to the physical properties of the cured films.

3. Radiation Cure Efficiency. The ultimate goal of radiation cure is to eliminate emissions entirely by providing 100% conversion of applied material to final product. For minimizing energy usage, this should be accomplished at the highest possible line speeds. Thus the definition of radiation cure efficiency must be related to measurements of both the energy input and the conversion of the formulation to non-volatile product.

Exposure of a material to EB radiation will deposit a measurable amount of energy, which is generally expressed in the units of Megarads, where 1 MR = 2.4 cal/gm. In typical application tests, the dose required for "cure" is determined observationally by running at various doses and testing for some physical property. The cure dose for coatings often refers to the minimum dose needed for a tack-free surface. This procedure is not meaningful if one desires to produce a fully polymerized material which is tacky, such as for an adhesive.

The exposure of a given formulation to EB radiation results in conversion of some fraction of the sample to a polymerized non-volatile film. The remainder of the sample is potentially volatile, either during the EB exposure or during subsequent treatment or usage of the final product. A straightforward gravimetric technique, in use in our laboratory for some time to measure the conversion of a formulation, is based on weighing the wet coating applied at the desired weight on a cleaned aluminum panel before EB exposure, after EB exposure, and after a post-bake of five minutes at 350°F. Reproducibility is generally within 1%.

The EB unit in use at the Mobil Chemical Company Edison Laboratory is a curtain-type laboratory electron processor which requires a waiting time of about one minute to reduce the oxygen level with nitrogen flushing. During this nitrogen flushing, a loss of volatile monomer can occur, which reflects a similar potential loss on high speed coating equipment. Low volatility monomers give negligible weight losses during flushing and EB exposure, so the measurement of the film weight is considered a very useful screening device in the development of high conversion EB formulations.

Separate measurements have also shown that the resinous components are virtually non-volatile when baked at 350°F for five minutes without EB exposure. However, the liquid monomeric components are completely volatilized in the bake, demonstrating that no thermal conversion occurs. Thus, the weight measurements described above provide a measure of the amounts of liquid components which are lost in the EB unit and, from the post-bake weight, the total conversion to a non-volatile film.

Measurement of conversions of various formulations at various EB doses can be used to rank the reactivity of the formulation. A particularly useful procedure has been to prepare a standard mixture of an acrylate resin with various reactive diluent monomers in order to compare the volatility and reactivity of new monomers. For these studies, a mixture of 40 weight % of a Bis-phenol A epoxy diacrylate resin with 60% of the test liquid monomer has proved convenient. A viscosity measurement of the mixture also provides information on the relative viscosity reducing ability of the test monomer. Illustrative examples of these measurements are shown in Table I and Figure 1. Note from these examples that a monofunctional monomer, Monomer B*, can be used to provide the low volatility and high reactivity typical of the multifunctional monomers, while also serving to reduce the crosslinking. Many other available monofunctional monomers are found to be either more volatile or less reactive than Monomer B.

The relative reactivities of various other resins, monomers and combinations of monomers have been measured in a similar manner. From this information, it was learned that many commercially available monofunctional monomers were not suitable for use in radiation curable formulations. Mobil Chemical Company has now developed several proprietary monofunctional monomers which provide low volatility, high reactivity and safe handling properties to fulfill these needs. In addition, other material suppliers have begun to make suitable monomers available, so the overall availability of materials for formulating has improved greatly within the last few years.

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*Proprietary Mobil monofunctional acrylate monomer.

Table I

Electron Beam Conversions of Standard Formulations

Formulation = 40 wt % Dow XD9002 Resin
60 wt % Test Monomer

	Visc.	5MR		2MR		1MR	
Monomer	cp	EB	Bake	EB	Bake	EB	Bake
TMPTA	1710	100	96	100	93	100	90
HDODA	75	100	99	100	92	100	85
Monomer B	380	100	98	100	94	100	89
IBOA	220	93	79	88	71	86	69
PEA	125	99	93	99	77	98	64

All conversions measured for thin films ($\sim$3mg/in^2) on aluminum panels using the Edison Lab curtain-type laboratory electron processor.

EB conversions include $\sim$1 min flushing with nitrogen gas.

Bake conversion is after 5 min at 350°F.

TMPTA = Trimethylol propane triacrylate.
HDODA = Hexanediol diacrylate.
Monomer B = Mobil acrylate monomer.
IBOA = Isobornyl acrylate.
PEA = Phenoxyethyl acrylate.

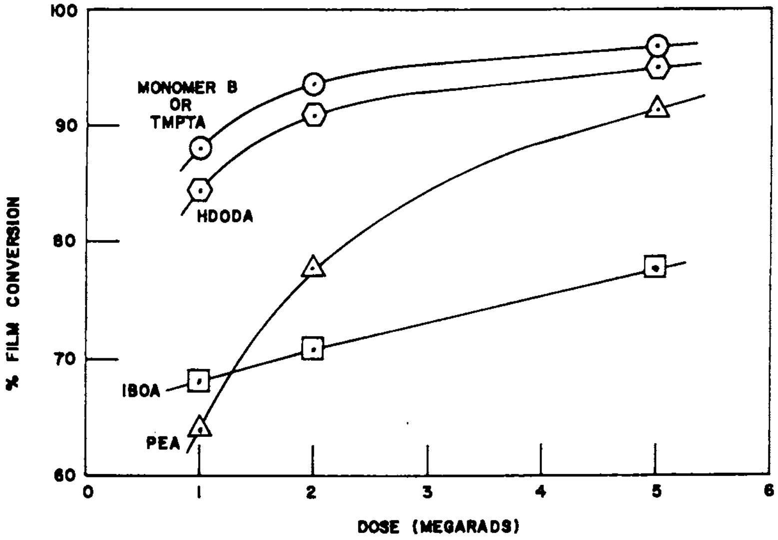

Figure 1. EB conversion with reactive acrylate diluents

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ACS Symposium Series; American Chemical Society: Washington, DC, 1979.

4. Safe Handling. Most of the handling problems associated with early radiation curable formulations have been traced to the liquid monomers in use. In particular, dermatitis has been a common complaint. As part of our monomer development program, extensive use of animal testing was made to further define acceptable monomers. At this time, the testing program, along with a limited amount of pilot and commercial line experience, indicates that the materials in use do not appear to pose health hazards any greater than the use of conventional coatings. However, as with any new technology, strict attention should be paid to adequate ventilation and minimizing of skin contact.

5. Application. From a formulation point of view, the key application parameter is rheology, which can be adjusted by the selection of resins and reactive diluents and their levels. EB curable formulations are available covering a range of 10 to 50,000 centipoise or higher.

6. Overall Economics. Statements are often made that radiation cure equipment requires too large a capital investment or that coating costs are too high. Our own analysis of many potential application areas indicates that radiation cure may be economically favorable for higher line speeds, heat sensitive substrates, replacement of conventional coatings presently used at less than 30% solids, and new products which cannot be made conventionally. For purposes of initial calculations, EB coating costs ranging from $1.50 to $2.50 per pound can be used to determine economic feasibility of possible new application areas.

7. End Use Properties. The areas of potential end use for radiation curable coatings and adhesives in industry may be as wide as those using solvents or water. In applications on porous substrates, such as paper, the rapid cure minimizes absorption into the substrate and can produce exceptionally high gloss with a minimum of coating usage. Other present commercial applications include clear and pigmented coatings for wood, paper and plastic films. Laminating adhesives have also gained acceptance in several specialty end uses. Coatings for metals, plastics and textile substrates are presently under development.

Control of the EB cured film properties through formulation is the key to meeting specific end use properties. A wide range of hardness and flexibility can be produced by adjustment of crosslink density and glass transition temperature. Studies on the effects of formulation variables on the tensile elongation properties of free films have proven especially valuable in development of coatings for flexible substrates.

By careful selection of materials used in EB curable formulations it has been found feasible to produce a wide range of physical properties while maintaining fast cure, safety in handling, smooth application, and reasonable cost.

B. Application Technology

The advancement of low viscosity, radiation curable systems in the last two years has for the first time made gravure application of these systems a reality. Since many industrial web processes (coating paper or film, laminating, metal coating, etc.) already employ gravure equipment, the availability of these new systems (1) has had major impact on the interest in electron-curing technology.

Prior to the development of low viscosity formulations (50-3000cp, depending upon pigment level, properties desired, cost, etc.), the handful of applications involving radiation cure coatings were performed with non-gravure equipment, i.e. reverse or direct roll coaters, curtain coaters or knife over roll coaters. For example, most UV curable wood fillers have been applied with direct roll coaters, reverse roll coaters or reverse roll fillers (2,3). The coating of vinyl floor tile, on the other hand, has traditionally used curtain coaters with good results, and a flocking operation employing an electron curable adhesive has successfully operated with a knife over plate (or roll) station (4). The use of these application techniques was generally necessary both because of the type of product being coated and the rather high viscosity (syrupy) nature of the coatings used. Moreover, some of the coatings required moderate heating to reduce the viscosity to a level where coating smoothness would show optimum results.

Now, however, gravure and offset gravure coating appear to be increasingly feasible for a wide variety of high speed web processes. Over the past year, many electron curable coatings and adhesives were successfully applied and cured on a specially built pilot coating/laminating line at speeds up to 280 meters/minute. This line, incorporating a very versatile coater with a curtain type EB curing station (5), is capable of applying materials with direct gravure, offset gravure, reverse offset gravure, as well as reverse roll and knife over roll. Most of the trials run to date, however, have utilized the first three techniques.

A major criterion for application is the achievement of a smooth, continuous surface, whether it be flat or glossy. Since there are no solvents or water in these materials for leveling by surface tension, the appearance of the 100% solids coating as it is applied is essentially the appearance of the cured finish.

To achieve the best finish, pilot experience has shown that offset gravure will consistently give a smoother surface than direct gravure for materials having viscosities in the upper part of the gravure range (∿500-3000cp). The difference between direct and offset gravure is shown in Figure 2. The improvement with offset is most likely due to the offset roll both smearing the gravure pattern (rolls can be operated at slightly different speeds) and splitting the coating film before it's transferred to the substrate. Better coating surfaces also result with offset gravure on many of the lower viscosity (∿500cp or less) formulations, but the appearance of "flooding" (Figure 3) gives rise to streaking problems and thus these materials cannot be applied with offset gravure. Whether or not such formulations give a satisfactory surface with direct gravure can only be determined by running them and observing the results. It has not yet been possible to directly relate viscosity with this flooding problem as the overall rheology of the material is what determines performance. Generally, however, the higher gravure viscosities do not show flooding, and offset gravure is the preferred coating technique when the smoothest possible surface is desired.

Reverse offset gravure has proven useful in applying certain coatings where forward offset gravure has shown problems with surface defects, i.e. fish eyes, streaks, pits, or roughness. In this case, as with reverse roll coating, the reverse wiping action of the offset roll provides enhanced smoothness. Our experience has shown this technique particularly useful in applying highly pigmented coatings to aluminum roll stock.

The use of any of these gravure coating methods can usually be enhanced by the addition of a rotating smoothing bar on the surface of the coated substrate just prior to cure. This device can smooth out many minor and sometimes major irregularities in the surface resulting from coating application. Usually the smoothing bar is rotated in the reverse or opposite direction the web is traveling to provide a wiping action. In some unusual cases, however, certain pigmented coatings give better results when the bar is rotated in the web direction at approximately the same surface speed. Other situations may also warrant the use of multiple smoothing bars of perhaps differing surface textures.

One of the advantages of using gravure or offset gravure is the ability of the technique to apply coatings of a uniform and consistent thickness. How much coating or adhesive is applied is primarily determined by the type and depth of the engraving on the gravure cylinder. Experiments with both direct and offset gravure on a wide selection of coatings indicate the following thicknesses result from quadrangular cell (6) engraved rolls:

200 Quad - ∿ 2- 4μ coating thickness
150 Quad - ∿ 5- 8μ coating thickness
110 Quad - ∿ 8-10μ coating thickness
85 Quad - ∿12-15μ coating thickness

The combination of electron curing with gravure application technology can offer some rather unusual benefits. One of the most important of these is the control of coating penetration into porous substrates by the very short dwell time between coating application and cure. With typical dwell times on the order of 0.5 sec or less, coatings can be deposited at minimum thickness on porous substrates such as paper while achieving maximum surface smoothness. Figures 4 and 5 show photomicrographs of a paper surface before and after coating by offset gravure. The EB cured coating thickness is approximately 5μ (150 Quad). Note the

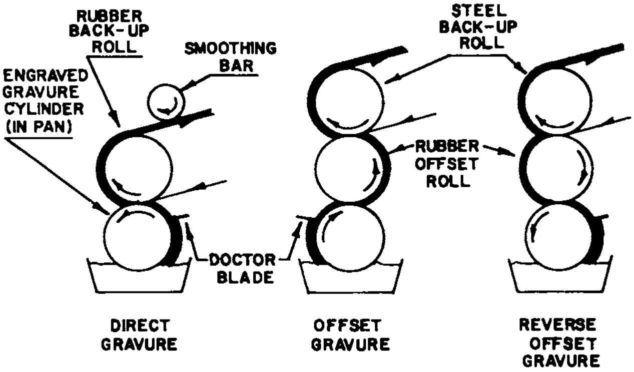

Figure 2. Gravure application technique

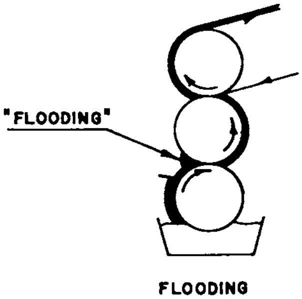

Figure 3. "Flooding" with offset gravue

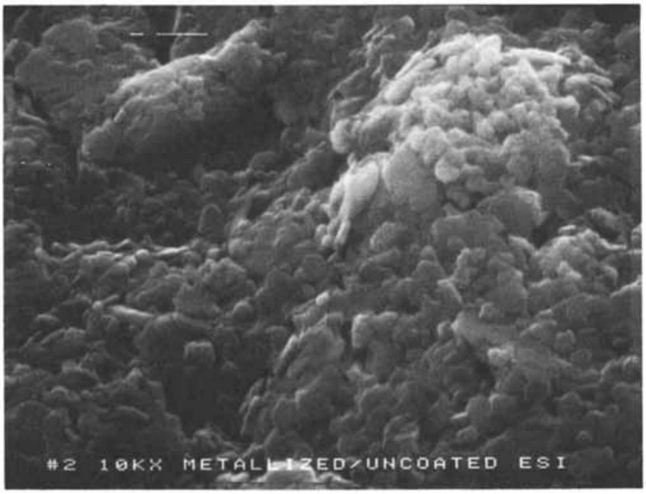

Figure 4. Photomicrograph (7200×) of 28# clay coated paper surface. Longer of two lines represents 1μ.

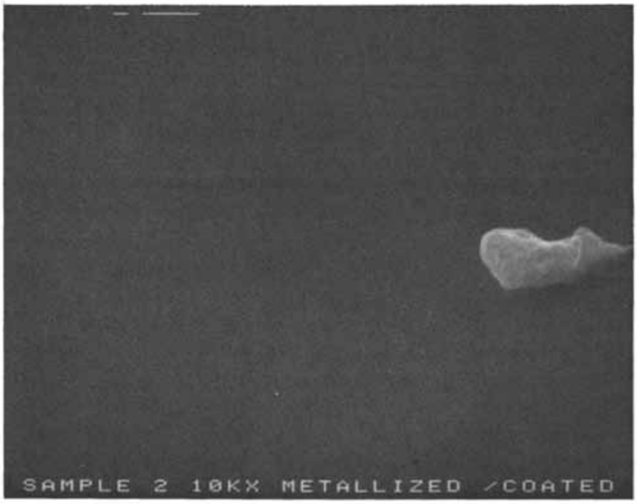

Figure 5. Photomicrograph (7200×) of same paper coated with approximately 6μ of an EB cured coating (applied offset gravure)

absence of surface deformities in the coating in spite of the rough nature of the original paper surface.

Since low viscosity electron curable systems have only recently become available, the application results presented here do not attempt to give all the answers. Each coating system has its own rheology and only by running actual coating trials can the performance of the application technique be evaluated. Perhaps, when enough data has been accumulated, accurate predictions on coating behavior will be routine matters. However, until that time is reached, general guidelines such as presented here will hopefully prove useful to those considering the adoption of electron curing technology.

References:

(1) Gerhardt, G. W., 3rd International Radiation Curing Conference, Session X, Paper FC76-531, Society of Manufacturing Engineers, Chicago, Sept. 28-30, 1976.
(2) Ibid, Jones, D. T., Session VII, Paper FC76-537.
(3) Ibid, Hodakowski, L. E., Session V, Paper FC76-502.
(4) Ibid, Trask, B. D., Session VIII, Paper FC76-521.
(5) Nablo, S. V. and Tripp, E. P., Radiation Physics and Chemistry, 9, 325, (1977).
(6) For more information see: Heurich, C. R., Better Ink Transfer Guaranteed by New Engineering Techniques, Report of Proceedings of Flexographic Technical Association Forum, 1966, May 10-11, 1966.

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Optimization of Cure Conditions During Processing of Acrylic Latex Coatings

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Thermosetting acrylic latexes are commonly used as vehicles for industrial water-borne coatings (1). These latexes contain polymers with reactive side groups (such as carboxyls, amides and hydroxyls) which serve to link the polymer chains together during "cure" - a process generally achieved by the application of heat to the coating. Crosslinking of the polymer chains results in a coating with superior physical and chemical properties (1-6). These properties are especially enhanced when the latex polymers are heated in the presence of crosslinking agents such as alkylated melamine formaldehyde compounds (4,5). The crosslinking reaction is catalyzed by the presence of acids (6,7).

The rate at which the crosslinking reaction occurs is of major interest to a coating manufacturer since it dictates the amount of energy and the time required to cure the coating to a set of desired physical properties. A number of physical methods for assessing the degree of crosslinking achieved during cure of acrylic polymers have been previously described (7,8). However, very little of the information generated in these studies can be directly applied by a coatings manufacturer to predict the conditions required to cure the coating during processing. A method for predicting cure conditions would be very useful to the coatings manufacturer since it will give him the flexibility of adjusting simultaneously the time and temperature for cure in such a way as to minimize the cost of production.

The studies reported in this paper were aimed at finding a relationship between time and temperature for cure of an acrylic latex coating system. Since the crosslinking reaction studied is an acid-catalyzed reaction (6,7), the effect of pH of the coating on the time-temperature relationship for cure was also studied. The situation of a coating being conveyed through an oven (set at a constant temperature) is analyzed to take into account the changing temperature of the coating with time. The analysis leads to a general procedure for predicting the conditions for cure of coatings during processing.

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Analysis

Definition of Minimum Cure Temperature (MCT). The word "cure" is used to describe the process by which polymer chains which contain reactive side groups are linked to each other, either with or without the aid of a curing agent (Figure 1a). When a sample of uncrosslinked polymer is placed in an oven, set at some elevated temperature, the number of crosslinks that are formed within the sample increases with time (Figure 1b). The rate at which this number increases is dependent on the oven temperature. Generally, this rate increases as the temperature increases (Figure 2).

When all possible crosslinking reactions within the polymer have been completed, the polymer is said to be "fully crosslinked" (Figure 1). Before this occurs, however, there is a point during the curing process when all the polymer chains are linked to each other by at least one crosslink. This point, called the "gel point" (Figure 1a) is usually characterized by the ability of the polymer sample to resist being dissolved by a good solvent. Since polymer chains in latexes are usually of high molecular weight, the number of crosslinks required to link all the chains together is small. Hence, gel point usually occurs quite early during the cure process (Figure 1b). This is in contrast to the cure of thermosetting resins such as alkyd (9) and epoxy (10) resins where the starting resin consists of multifunctional monomers and "cure" involves linking these monomers to form a relatively tight network. Gel point in these resins occur quite close to the point where all the crosslinking reactions have been completed (9, 10).

The temperature required to cure a polymer to its gel point, for an arbitrarily set cure time, is defined here as the "Minimum Cure Temperature" or MCT. Figure 2 illustrates the fact that if the cure rate increases with temperature, then MCT decreases as the cure time increases. Note that the definition of MCT here assumes that the polymer increases in temperature to its cure temperature instantaneously at the beginning of "cure" and that this temperature is maintained throughout the cure time. This is certainly not true in a situation where the coating, applied to a substrate, is conveyed through an oven. The temperature of the coating, in this case, increases with time in the oven and may never reach the oven temperature as it exits from the oven. The use of the term, MCT for curing under such a situation is ambiguous. To avoid this ambiguity, a method for determining cure has been developed in our laboratory, where the coating temperature increases almost instantaneously to its cure temperature. The use of MCT will be restricted exclusively to this method of determining cure (see Experimental Section).

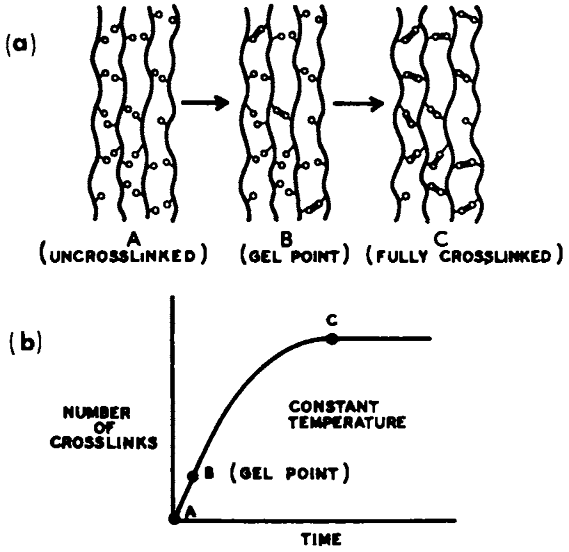

Figure 1. (a) Diagram of the "cure" of coatings: (○) reactive groups and (▬) crosslinks; (b) number of crosslinks formed vs. time during the "cure" process.

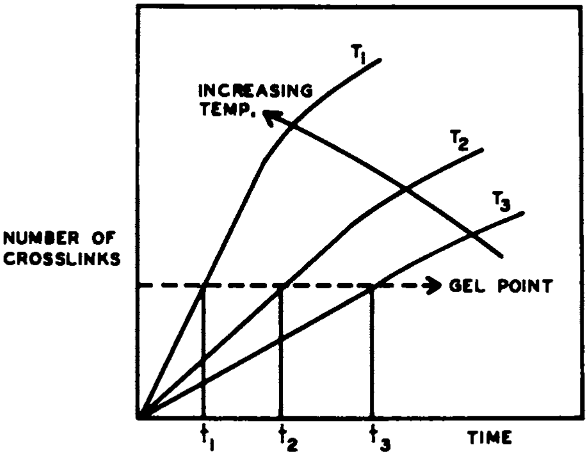

Figure 2. Number of crosslinks formed (n) vs. time during "cure" of coatings at various temperatures. For cure times, t_1, t_2, and t_3, the corresponding minimum cure temperatures are T_1, T_2, and T_3.

In Energy Conservation in Textile and Polymer Processing; Vigo, T., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 1979.

Solution of the Rate Equation for Cure. The rate at which crosslinks are formed is given by:

$$\frac{dn}{dt} = k\ f\ (n) \qquad (1)$$

where k is the overall rate constant and f (n) is some function of n, the number of crosslinks formed at time, t. For the purpose of this analysis, it is not necessary to know what form f (n) takes. The only assumption made is that this function does not change as the crosslinking reaction proceeds.

The integrated form of Equation 1 takes the form:

$$F\ (n) = \int_0^t k\ dt \qquad (2)$$

where F (n) is another function of n. Solution of the integral in Equation 2 requires a knowledge of the overall rate constant, k, which may vary with time.

In the case where the reaction is catalyzed by a strong acid, the overall rate constant can be considered (11) to be the sum of two rate terms:

$$k = k_N + k_C \left[H^+\right] \qquad (3)$$

where k_N is the rate constant for the reaction in an uncatalyzed system and k_C is the rate constant for the reaction in the presence of a strong catalyst. Assuming the approximate relationship between the hydrogen ion concentration and the pH of the solution (12), Equation 3 can be written as:

$$k = k_N + k_C\ 10^{-pH} \qquad (4)$$

If we now assume that each of the rate constants, k_N and k_C vary with temperature according to the Arrhenius relationship, Equation 4 then becomes:

$$k = A'_N\ e^{-E_N/RT} + A'_C\ 10^{-pH}\ e^{-E_C/RT} \qquad (5)$$

where E_N and E_C are activation energies and A'_N and A'_C are the collision factors associated with each of the rate terms.

Substituting Equation 5 into Equation 2 produces the equation:

$$F(n) = \int_0^t \left[A'_N e^{-E_N/RT} + A'_C\ 10^{-pH} e^{-E_C/RT}\right] dt \qquad (6)$$

Equation 6 can be used to predict the time, t required to cure a coating to a predetermined set of physical properties, corresponding to a certain number of crosslinks, n in the coating. In order to solve the equation, it is necessary to determine how the pH and the temperature of the coating vary with time. If the coating does not contain any volatile acid or base, the pH of the coating can be considered to be a constant (see Discussion Section). The solution of Equation 6, then, depends on the variation of the temperature of coating with time. Two special cases will be considered below:

Case 1: $T = T_C$, a constant; $n = n_g$, the number of crosslinks required to bring the polymer to gel point. This corresponds to the conditions used to determine MCT, as defined above and hence, T_C is equivalent to MCT. Solution of Equation 6 is simple in this case since the integrand is now a constant, and can be taken out of the integral to give the result:

$$\frac{1}{t} = A_N e^{-E_N/RT_C} + A_C 10^{-pH} e^{-E_C/RT_C} \tag{7}$$

where

$$A_N = A'_N/F\ (n_g) \tag{8}$$

and

$$A_C = A'_N/F\ (n_g) \tag{9}$$

For reactions occurring in the uncatalyzed latex polymer, the first term on the right hand side (RHS) of Equation 7 predominates so that:

$$\frac{1}{t} = A_N e^{-E_N/RT_C} \tag{7a}$$

When the latex is highly acidified (to below pH 3.5), the second term on the RHS of Equation 7 predominates so that:

$$\frac{1}{t} = A_C 10^{-pH} e^{-E_C/RT_C} \tag{7b}$$

By determining MCT as a function of cure time under these two extreme conditions, it is possible to estimate the values of A_N, A_C, E_N and E_C from Arrhenius plot of Equation 7a and 7b (see Results Section).

Case 2: $T = T\ (t,T_s)$, $n = n_w$, where $n_w > n_g$. In this case, the coating temperature is a function of both the time, t, in the oven and set oven temperature, T_s. The number of crosslinks formed, n_w is greater than that required to reach gel point.

Solution of Equation 3 under these conditions give:

$$\int_0^t \left[A_N e^{-E_N/RT(t,T_s)} + A_C 10^{-pH} e^{E_C/RT(t,T_s)} \right] dt = C_w \qquad (10)$$

where $C_w = F(n_w)/F(n_g)$. To solve Equation 10, it is necessary to know the function, $T(t,T_s)$ and the magnitude of C_w. An expression for $T(t,T_s)$, in the case of a thin substrate passing through an oven, set at a constant temperature, will be described in the next section.

Variation of Substrate Temperature with Cure Time. For a thin substrate placed in an oven, set at a constant temperature, T_s, the transient temperature, T, of the substrate is given (13) by:

$$h\ (T_s - T)\ S = m\ C\ \frac{dT}{dt} \qquad (11)$$

where h is the heat transfer coefficient, S is the surface area, m is the mass and C is the specific heat of the substrate.

Solution of Equation 11 using the appropriate boundary conditions gives:

$$T\ (t,T_s) = T_s - (T_s - T_o)e^{-Bt} \qquad (12)$$

where

$$B = \frac{hS}{mC} \qquad (13)$$

and T_o is the initial temperature of the sheet. The value of B is generally not a constant (13) but is dependent on the variation of the specific heat, C, with the set oven temperature, T_s. An empirical relationship was established between B and T_s in the present study (see Results Section).

Computer Solution of the Cure Rate Equation. Solution of Equation 10 requires a numerical integration method which involves the use of a computer. A program, in Fortran, was written on a Xerox Sigma 9 computer to perform the necessary numerical integration. The program consists of two parts. The first part allows the computation of the value of C_w for a given set of oven temperature, pH level and cure time, t_c. The second part of the computer program allows the computation of the cure time, t_c, for a given oven temperature setting, pH level and a predetermined value of C_w.

In order to use the program to predict the conditions for cure of a coating during processing, the values of A_N, A_C, E_N,

E_c are first determined using MCT measurements, as described above. Next, the variation of the coating temperature with time and oven temperature setting, $T(t,T_s)$ is determined (Equation 12). Finally, one set of conditions (t_c, pH and T_s) required to cure the coating to the desired physical property is determined.

All the information obtained can then be fed into the first part of the computer program to obtain the value of C_w corresponding to the desired physical property. Once the value of C_w is obtained, the second part of the computer program can be used to predict the time, t_c required to cure the coating at any other pH level and oven temperature setting.

Experimental

Determination of MCT. The coating system used consists of a thermosetting acrylic latex, Hycar 2600X256 (BFGoodrich Chemical Division) containing 15 wt.% of a partially methylated melamine formaldehyde, Cymel 373 (American Cyanamid Corporation). Adjustment of the pH level of the coating was achieved by the addition of p-toluene sulfonic acid.

After adjustment of the coating to the desired pH, a thin film was cast on a 0.025 inch X 3 inch X 12 inch aluminum panel by means of a draw bar having a 0.002 inch clearance. The aluminum panel was then placed on the heating block of an equipment which is similar to the one described by Protzman and Brown (14) for determining the minimum film formation temperature of coatings. The heating block has a cold temperature at one end and a high temperature at the other. This temperature gradient is maintained by a series of individually controlled heating elements (embedded in the heating block) and a series of individually controlled channels for the passage of a coolant flowing from a low temperature bath. By adjusting the power settings of the heating elements and the controlling valves to the cooling channels, a wide range of temperature gradients can be obtained.

Embedded in the heating block are a series of thermocouples which are located one inch apart along the length of the heating block. These thermocouples are connected to a multi-channel thermocouple indicator (Type J, DS-500, Doric Scientific Corporation, San Diego, California), which provides a digital readout of the temperature at each point, one inch apart, along the heating block. Temperatures between these points were determined by interpolation.

The aluminum panel with the thin coating on top of it was placed on the heating block for a set period of time (usually from 1 to 8 minutes). The panel was then removed and placed on a cool metal surface which serves as a heat sink to bring the panel back to room temperature almost instantaneously. The panel was then placed in a good solvent for the coating. For the coating studied, a good solvent was found to be methyl-ethyl ketone (MEK) containing 5 wt.% of distilled water.

The panel was placed in the solvent for 4 minutes, during which time the solvent dissolved away the uncured portion of the coating, leaving the cured portion intact on the panel. The former portion corresponds to the portion of the coating which was placed at the lower temperature end of the heating block while the latter portion corresponds to the portion placed at the higher temperature end. The line which separates the cured and the uncured portion is generally quite sharp. To aid in the visualization of this line, a Fastolon bright blue dye (081-2550, Allied Chemical Corporation, Morristown, New Jersey) was added to the MEK/water solvent. The dye penetrates the cured portion of the coating, causing the line which separates it from the dissolved portion to be enhanced. The temperature on the heating block corresponding to this line was taken as the minimum cure temperature.

Cure Studies with Coated Hardboard in an Infrared Oven. A thin film of the coating was applied on a 1/8th inch thick primed hardboard using a wire-wound rod. The coated board was passed through an infrared (IR) oven by means of a conveyor belt. Three different oven temperature settings, 157°C, 180°C and 198°C, were used for the study. The speed of the conveyor belt could be varied to give residence times in the oven of 0.5 to 5 minutes. The board surface temperature (BST) of the coating as it passed through the oven was determined for various oven temperature settings and conveyor belt speeds. This was done by embedding a thermocouple at the board surface before application of the coatings and recording the temperature on a strip chart recorder as the coated board passed through the oven.

For each oven temperature setting, the residence required to produce a "cured" coating was determined. "Cure" was determined by a block resistance test. Two coated board samples exiting from the oven were allowed to cool to 66°C and then pressed together face-to-face in a heated press (66°C) set at a pressure of 80 psi. After 10 minutes, the boards were removed from the press and separated from one another. The coatings were considered "cured" if no blocking occurred.

Results and Discussion

MCT Measurements. The MCT of the acrylic latex coating was measured for a number of pH levels and times on the heating block. Figure 3 shows that for the coating at neutral pH (Figure 3a) and at low pH (Figure 3b), the cure time versus MCT follows an Arrhenius relationship. This is in agreement with the analysis given above (see Equations 7a and 7b). From the Arrhenius plot at neutral pH (Figure 3a), the values of A_N (1.603×10^{10} min.$^{-1}$) and E_N (17.9 K cal/mole) were determined. Similarly, from the Arrhenius plot at low pH (Figure 3b), the values of A_C (9.905×10^{13} min^{-1}) and E_C (16.03 K cal/mole) were determined.

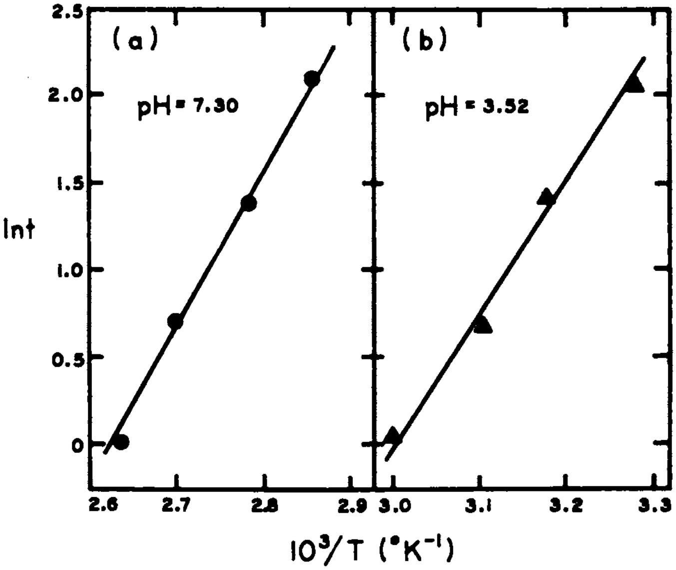

Figure 3. Arrhenius plots of cure time (t) vs. minimum cure temperature (T) for coatings at (a) pH 7.30 and (b) pH 3.52

Once the values of A_N, A_C, E_N and E_C are determined from the data at the neutral and low pH, Equation 7 allows the prediction of MCT for any other cure time at any intermediate pH levels of the coating. In order to test the validity of this equation, the predicted value of MCT are plotted as continuous lines in Figure 4 and compared with some experimental points. There appears to be a good correlation between the theoretical and experimental results.

The above results illustrate the advantage of using the MCT method for studying the cure of coatings. The equipment used is simple and inexpensive and the MCT can be determined very rapidly. A knowledge of the kinetics of the crosslinking reaction (f(n) in Equation 1) is not required so that the usually time-consuming process of determining the rate constants, typical of most kinetic studies, is avoided. By determining the MCT vs. cure time for the coating at only two pH levels (neutral and low), the values of A_N, A_C, E_N and E_C can be determined. These four constants provide a full characterization of the relationship between the cure time, cure temperature and pH of the coating (Equation 7, Figure 4).

There are, however, a number of disadvantages in the use of the MCT method. The measurement of MCT is dependent on the availability of a "good" solvent to dissolve away the uncured portion of the coating. Although in the present study, there was no problem in identifying an appropriate solvent, it is possible that, for some coating systems, this may present a problem. We have found that, in some cases, a good solvent would cause the cured portion of the coating to swell quickly and detach itself from the panel, leaving a tacky uncured portion on the panel. This effect could be confusing to an inexperienced observer who expects the uncured portion to dissolve into the solvent. In any case, the demarcation between the cured and uncured portions is still sharp under these circumstances and the MCT can still be determined quite accurately.

Another drawback of the MCT method is the fact that determination of MCT is obtained under conditions where the coating reaches its cure temperature almost instantaneously and maintains that temperature throughout the time of cure. In actual processing, the coating temperature changes with time in the oven. Hence, it is not possible to use the time-temperature relationship for cure of the coating, as determined by the MCT, to directly predict the conditions for cure of the coating in industrial processing.

Furthermore, the criterion for cure in MCT determination is the attainment of gel point (Figure 1). For most industrial coatings, the number of crosslinks required to obtain the desired physical properties is much greater than that attained at gel point. The purpose of the analysis given earlier (Case 2) is to take into account the changing temperature of the coating as it passes through the oven,and the higher crosslink density required

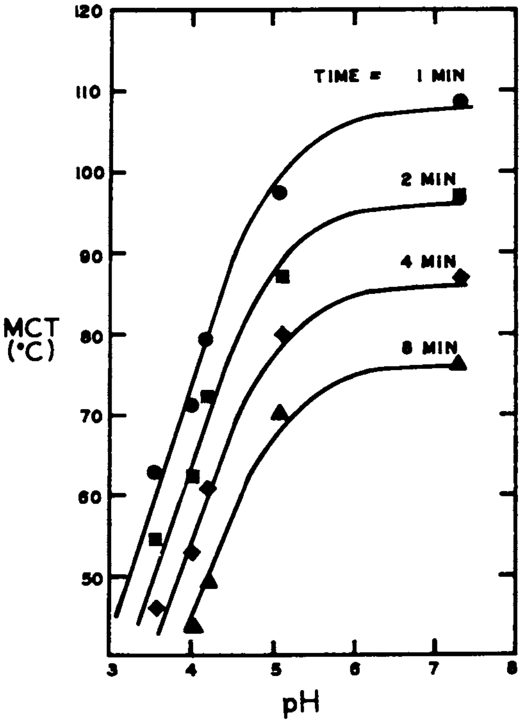

Figure 4. Comparison of theoretical prediction and experimental results of MCT vs. pH coatings at various cure times. The solid lines represent plots of Equation 7.

to obtain the desired physical property. The use of this analysis for the cure of a coating under conditions similar to those met in industrial processing is illustrated in the next section.

Cure of the Coating in an Infrared Oven. The acrylic latex coating was applied on a primed hardboard and cured by passing it (with a conveyor belt) through an infrared oven. By adjusting the belt speed and the infrared oven temperature setting, different degrees of cure could be obtained in the coating. The temperature of the coating, as it passed through the oven, was found to vary with the oven temperature setting, T_s and the residence time in the oven according to Equation 12 (see Figure 5). The value of B (in Equation 12) needed to provide a good fit of the experimental results shown in Figure 5 was found to vary with T_s according to the relationship:

$$B = 0.002204 \times T_s - 0.148 \qquad (14)$$

The time required to cure the coating to obtain block resistance at various oven temperature settings and pH of the coating were determined. The results are listed in the fourth column of Table 1. The data from the first set of cure conditions listed in Table 1 was used to compute the value of C_w (Equation 10), using the computer program described earlier. This value of C_w (= 10.12) corresponds to the degree of crosslinking which must be attained at any other cure conditions in order to obtain equivalent block resistance. Using this value of C_w in Equation 10, the second part of the computer program can be used to predict the time required to cure the coating at other oven temperature settings and pH of the coating. The predicted cure times for all the other conditions shown in Table 1 are listed in the last column of the table to allow comparison with the experimentally determined cure times.

TABLE I.
Comparison of Experimental and Theoretical Time for Cure in IR Oven

IR Temp Setting (°C)	pH of Coatings	Exiting BST (°C)	Expt. Cure Time (min)	Predicted Cure Time (min)
198	7.0	149	4.32	---
	5.0	138	3.75	3.86
	4.0	122	2.82	2.71
	3.0	90	1.60	1.58
180	5.0	135	4.96	5.00
	4.0	114	3.42	3.42
	3.0	86	1.92	1.95
157	4.0	108	4.72	4.86
	3.0	79	2.82	2.66

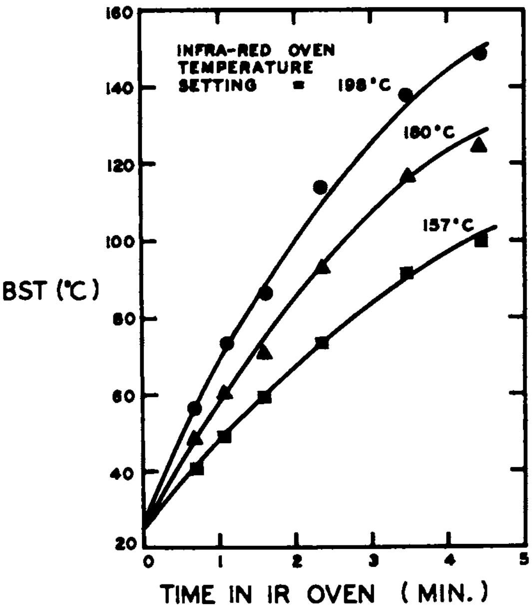

Figure 5. Plot of the board surface temperature (BST) vs. residence time in IR oven. The solid lines represent plots of Equation 12.

The excellent agreement between the experimental and the theoretical cure times (Table 1) is, to some extent, surprising in view of the number of simplifying assumptions made in the analysis. The assumption that the pH of the coating is constant throughout the cure process is not strictly valid. The pH of the coating is expected to change as the coating becomes more concentrated during drying. However, the initial pH of the coating gives a measure of the initial concentration of hydrogen ions in the coating. Since the catalysis of the crosslinking reaction is dependent on the complexing of these ions to reactive groups of the polymer (6), the extent of catalysis is probably dependent on the initial ratio of hydrogen ions to reactive groups. This may explain why the initial pH of the coating can be used in Equation 10 to predict the cure times.

The assumption that the function, f(n) in Equation 1 is constant throughout the cure process may also be open to question. This assumption is equivalent to stating that the kinetics of reaction is such that the order of reaction does not change as the crosslinking reaction proceeds. This may be correct only if one species of reactive group is present in the coating. Since the coating used in the present study contains both latex polymers and curing agents, three types of reactions (polymer-polymer, curing agent-curing agent, and polymer-curing agent) are possible. The fact that the experimental results do not indicate a change in f(n) with time suggests that one of these reactions probably dominates over the other two. Previous studies using very similar coating systems (6) suggest that the polymer-curing agent reaction may be the dominant reaction.

Finally, the assumption that the physical properties of the coating is dependent only on the degree of crosslinking is not strictly correct. Other factors, such as fusion of the latex particles and adhesion of the coating to the substrate may have a strong effect on the final properties of the coating. It may, therefore, be fortuitous that the criterion used for cure in this study, namely, block resistance of the coating, is predominantly dependent on the degree of crosslinking. The use of other criteria, such as stain resistance or mar resistance may not produce as good a correlation between experimental and theoretical results.

The analysis outlined in this paper has been applied to the cure of acrylic latexes used as binders for nonwoven (15). The criterion used for cure in that study was the wet tensile strength of the nonwoven, bonded with the latex binder. A good correlation was obtained between the experimental and theoretical cure conditions as long as the pH of the latex binder was not too low. Deviations from the theory under the latter conditions can be explained by the fact that the cellulosic fibers were being degraded by a combination low pH and heat. Some preliminary results in our laboratory suggests that this may also occur in board coating if the pH of the coating is low enough (less than 2.0).

Summary

In spite of a number of simplifying assumptions made in our analysis, the experimental results seem to indicate that the analytical approach described in this study can be used to predict cure under conditions similar to those met in normal industrial processing of the coating. Such an approach would allow the coatings manufacturer more flexibility in the choice of cure conditions (oven temperatures and belt speeds). By determining the contribution of production time and energy cost to the economics of production, it should be possible to incorporate results from this kind of analysis into an integrated approach to optimize conditions for cure of the coating.

Acknowledgement

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Literature Cited

1. Warson, H., Emulsion Polymerization (I. Pirma and J. L. Gardon, eds.), ACS Symposium, Series 24, 1975; pp. 330.
2. Yeliseeva, V. I., Br. Polym. J., (1975), 7, 33.
3. Kamogowa, H., and Sekiya, T., J. Poly. Sci., (1961), 1, 211.
4. Koral, J. N. and Petropoulos, J. C., J. Paint Tech., (1966), 38, 600.
5. Blank, W. J. and Hensley, W. L., J. Paint Tech., (1974), 46, 47.
6. Saxon, R. and Lestienne, F. C., J. Appl. Polym. Sci., (1964), 8, 475.
7. Lewis, S. N., J. Paint Tech., (1966), 38, 667.
8. Janacek, J. and Hrouz, J., J. Poly. Sci.: Symposium, (1975), 53, 283-290.
9. Bobalek, E. G., Moore, E. R., Levy, S. S. and Lee, C. C., J. Appl. Polym. Sci., (1964), 8, 625.
10. Dusek, K. and Ilavsky, M., J. Poly. Sci.: Symposium, (1975), 53, 29-44.
11. Kilpatrick, M., Advances in Catalysis (W. G. Frankenburg, V. I. Komarewsky and E. K. Rideal, eds.), Academic Press, Inc. New York, N.Y., (1954), 6, 241-270.
12. Kolthoff, I. M. and Laitenan, H. A., pH and Electrotitrations, Wiley, New York, N.Y., 1941.
13. Rohsenow, W. M., Hartnett, J. P., Eds., Handbook of Heat Transfer, McGraw-Hill Book Company, New York, N.Y. pages 3-26, 1973.

14. Protzman, T. F. and Brown, G. L., J. Appl. Polym. Sci., (1960), 4, 81-85.
15. Huang, C., International Nonwovens and Disposables Association, Fifth Technical Symposium Meeting, Washington D.C., Symposium Papers, pages 81-106, March, 1977.

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9

New Energy Saving Reactive Acrylic Liquid Polymers for the Pressure Sensitive Adhesives Industry

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A large volume of solution adhesive is consumed in the pressure sensitive adhesive (PSA) converting industry. This requires vast quantities of energy for drying and for incineration or solvent recovery. The well-publicized natural gas shortage of the winter of 1976-1977, the energy crisis, and the tightened EPA emission control regulations make the solventless and high solids PSA systems very attractive.

Recently, hot melt PSA systems have been introduced and radiation curable PSA systems are at the commercial development stage. High solids (50%-70% by wt.) nonaqueous dispersion acrylic PSA systems have also been reported(1). Unlike the hot melt and radiation cured systems which require new capital outlay in coating head and/or curing (drying) equipment, BFG has developed PSA systems, based on Hycar® 2100R reactive acrylic liquid polymers and isocyanate terminated prepolymer, which can be processed at 80% solids (by wt.) with equipment presently used in the PSA industry, namely, the reverse roll and knife-over-roll coater.

Results and Discussion

Emission and Economic Advantages. The use of Hycar 2100R series polymers offers a significant reduction in solvent emission over conventional 40% solids system (by wt.). An 83% reduction in solvent emission (figure 1) results when the 80% solids Hycar system is used. Further reduction is obtained for 90% and 100% solids systems. The solvent content of the 90% solids system is so low that neither incinerator nor heat exchanger may be needed - a very good possibility for smaller PSA converters.

Figure II shows a comparison of the energy needed and energy cost for a system using a solvent incinerator with a heat exchanger if needed. The energy needed to make 1000 m^2 of adhesive

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is about 2.1X10^9 Joules for 40% solids conventional system and is about 3.5X10^8 Joules for the 80% solids system. This is about an 80% energy saving for the 80% solids system when compared with

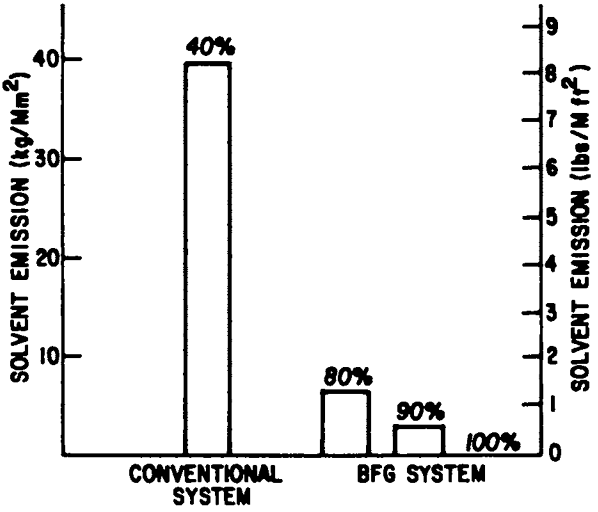

Figure 1. Effect of total solids on solvent emission

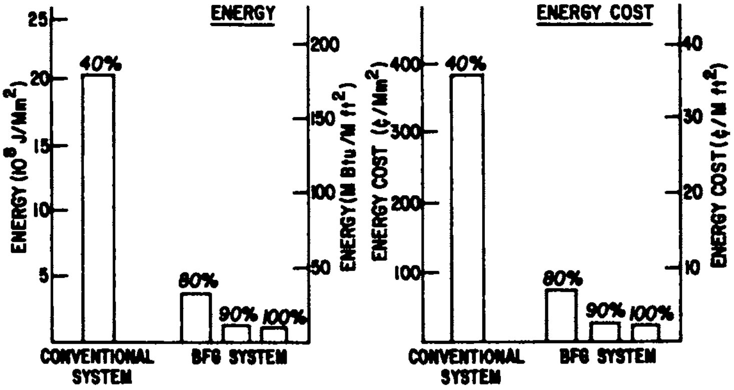

Figure 2. Energy and energy cost with incinerator and heat exchanger (if needed)

the 40% conventional system. Based on a natural gas price of \$2.00/1000 ft.^{3}, it would cost almost \$4.00 to make 1000 m^2 of adhesive for the 40% solids system and only about \$0.80 for the 80% solids system. The savings in energy and energy cost would, of course, be even higher for the 90% and 100% solids systems. Figure III shows the same comparison when no pollution control system is incorporated. A substantial reduction in energy usage and energy cost can be realized by the high solids or 100% solids system. The model that was chosen for the calculations is the following:

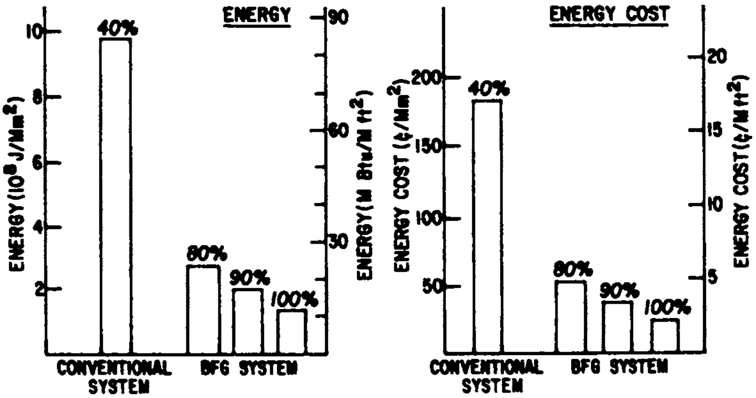

Figure 3. Energy and energy cost without pollution control

% Solids of conventional system by wt.	40
Dry adhesive film thickness	0.025 mm (1 mil)
Substrate	0.05 mm (2 mils) Mylar
Solvent	toluene
Specific gravity of adhesive	1.05
Line speed of coater	1.5 m/s (300 fpm)
Web width	1.52 m (60")
Oven length	45.7 m (150')
Oven width	3.1 m (10')
Oven height	3.1 (10')
Oven temperature	149°C (300°F)
Combustion efficiency	65%
Heat exchanger efficiency	43%
Natural gas cost	\$7.06X10^{-5}/1 (\$2.00/M ft^3)

Note that the difference in capital and operating costs between the conventional system and the BFG 80% solids and 90% solids systems due to the size difference of the pollution control equipment has not been considered, and that none of this equipment is needed by the 100% solids system. Also note that the energy cost calculations are based on natural gas. If oil or electricity is used, the cost would be even higher. Owing to the natural gas shortage, a number of converters have switched from natural gas to oil, thus the difference in energy cost of using oil is about twice that of using natural gas.

Materials. This paper is mainly concerned with two Hycar 2100R polymers, Hycar 2103 and Hycar 2106. These are characterized in Table I. Isocyanate Prepolymer C is used as the curative. Its typical properties are summarized in Table II.

TABLE I - Typical Properties of Hycar 2100R Polymers

	Hycar 2103		Hycar 2106	
	100% Solids	70% Solids	100% Solids	70% Solids
Appearance	Clear;Light Yellow	Clear;Light Yellow	Clear;Light Yellow	Clear;Light Yellow
Sp. Gr. @ 24°C	1.05	0.996	1.05	0.996
OH Value, meq./g.	0.53	0.37	0.75	0.53
OH Number, mg KOH/g	30	21	42	29
Viscosity Brookfield Pa·s (cps), @ 24°C	700(7x10^5)	1.7(1700)	400(4x10^5)	0.9(900)
Flash Point, °C	---	7	--	8

TABLE II - Typical Properties of Isocyanate Prepolymer C

Free NCO, wt. %	4.3-4.7
Sp. Gr. @ 24°C	1.09
Viscosity, Brookfield, Pa·s (cps), @ 24°C	24 (24000)

PSA Formulation and Properties. The formulations used in this study for the Hycar 2103-Prepolymer C and Hycar 2106-Prepolymer C PSA contain OH/NCO ratios of 1.7 and 1.3, respectively. Dibutyltin dilaurate catalyst is used at a 0.2 wt.% level based on the total adhesive solids. PSA samples are made from an 80% solids solution (by wt.) with a dry solvent system (27/73 by wt. of ethyl acetate-toluene) and cured at 150°C for 45 seconds. The samples are then evaluated by running 180° peel, static shear, rolling ball tack, and vinyl film shrinkage tests.

These adhesive systems give an excellent combination of static shear (at both room temperature and 70°C) and rolling ball tack along with excellent vinyl film shrinkage resistance. The results of these tests are summarized in Table III.

TABLE III - Typical PSA Properties

	Hycar 2103	Hycar 2106
Adhesive Film Appearance	Clear,Colorless	Clear,Colorless
180° Peel Strength[1,2], N/m (oz./in.)	438 (40)	569 (52)
Static Shear[1,3], h, 70°C	>100 (no creep)	>100 (no creep)
24°C	>1000 (no creep)	>1000 (no creep)
Rolling ball tack[1,4], cm (in.)	2.3 (0.9)	2.8 (1.1)
Vinyl Film Shrinkage[5], cm	0x0	0x0

[1] Test with 1-mil adhesive coating on 2-mil Mylar.

[2] PSTC-1, overnight dwell on SS panel.

[3] PSTC-7, 6.45 cm^2 (1 inch^2) contact area on SS panel, 1 Kg load.

[4] PSTC-6

[5] 5-mil vinyl film used, test run for 24 h at 70°C - 10.16 cm x 10.16 cm (4"x4") samples used.

Performance Flexibility. Figure IV illustrates the effect of the OH/NCO ratio of 180° peel strength and rolling ball tack for both the Hycar 2103-Prepolymer C and Hycar 2106-Prepolymer C adhesive systems. Peel strength values of 493 N/m (45 oz./in.) or lower are possible for the Hycar 2103 system simply by altering the OH/NCO ratio. Likewise for the Hycar 2106 system, peel strengths of 657 N/m (60 oz./in.) or lower are possible. In both cases, rolling ball tack remains relatively constant unless the OH/NCO ratio becomes too low. In addition, no creep in static shear is observed at room temperature or 70°C at the ratio shown.

High peel strength with cohesive failure is possible by increasing the OH/NCO ratio. At a higher ratio, slight creep is observed at room temperature in the static shear test. OH/NCO ratios above 2.0 for Hycar 2103 and 1.8 for Hycar 2106 result in adhesives having incomplete cures with low peel values and poor static shear strength.

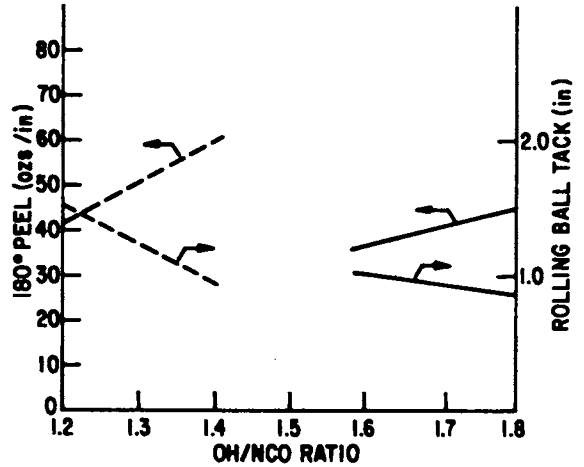

Figure 4. PSA properties vs. OH/NCO ratio: (——) Hycar 2103; (– – –) Hycar 2106.

Figure V demonstrates the effect of adhesive dry coating weight on 180° peel strength and rolling ball tack with OH/NCO ratios of 1.7 and 1.3 for Hycar 2103 and Hycar 2106, respectively. Static shear tests run both at room temperature and 70°C show no creep for both systems throughout the thickness range tested. Only at low adhesive coating weight does the rolling ball tack begin to increase slightly.

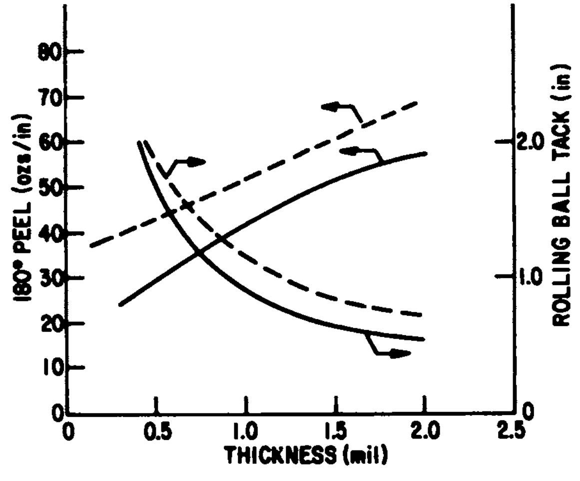

Figure 5. PSA properties vs. adhesive thickness: (——) Hycar 2103, OH/NCO = 1.7; (– – –) Hycar 2106, OH/NCO = 1.3.

Processing. The 80% solids systems are compatible with conventional coating equipment such as knife-over-roll and reverse roll. Prior to coating, the use of in-line metering-mixing equipment is recommended to accommodate the mixing of the 2-component system. A 90% solids Hycar 2106-based PSA system has been successfully processed by a reverse roll coater incorporated with a Twinflo® metering-mixing equipment (manufactured and sold by Liquid Control Corp. of Wickliffe, Ohio). Encouraging results have also been obtained by processing a solventless Hycar 2100R PSA system with a differential roll coater (manufactured by Egan Machinery Co.). The ratio of the Hycar 2100R polymer to isocyanate prepolymer can be adjusted to give a family of products with a range of peel strengths while retaining excellent static shear strength and tack (see Figure IV). This family of products can be produced at the "touch of a dial" with in-line metering-mixing equipment. The catalyst may be added to the Hycar 2100R polymer before mixing; however, a prolonged storage of Hycar 2100R polymer with catalyst should be avoided.

Figures VI and VII illustrate the initial viscosity of both the Hycar 2103 and Hycar 2106 systems as well as the viscosity increase with time due to the reactive nature of the 2-component system. These figures will help in determining the percent solids necessary for processing on a given piece of equipment depending upon its viscosity handling capability. Since the 100% solids PSA systems have high initial viscosities of over 100 Pa·s (100,000 cps), the conventional knife-over-roll and reverse roll coaters can not process them.

Curing occurs at elevated temperatures as the solvent is being evaporated. Various oven temperatures and air velocities can be used depending on the substrate being coated. The curing temperature vs. curing time is summarized in Table IV. If desired, partial curing may be performed in the oven and then completed in the roll.

TABLE IV - Curing Temperature vs. Curing Time

	Curing Time	
Curing Temp.	Hycar 2103/ Prepolymer C	Hycar 2106/ Prepolymer C
150°C (302°F)	45 sec.	30 sec.
120°C (248°F)	1.25-1.5 min.	1 min.
93°C (200°F)	4 min.	2.5 min.

Acetates, such as ethyl acetate and 2-ethoxyethyl acetate, hydrocarbons, such toluene and heptane, chlorinated hydrocarbons, such as methylene chloride and 1,1,1-trichloroethane, and mixtures of them, such as the mixture of toluene and ethyl acetate have been screended as solvents for the Hycar 2100R-based PSA. Good PSA properties are obtained using any of these solvents. How-

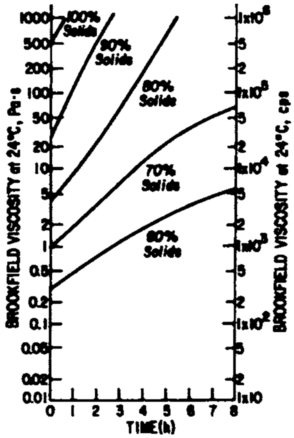

Figure 6. Effect of time on viscosity of Hycar 2103/Prepolymer C adhesive

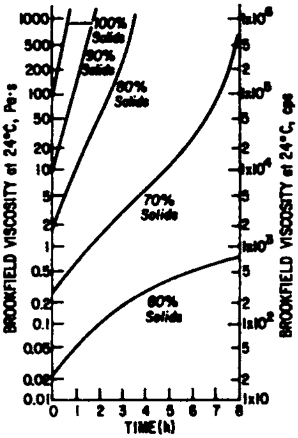

Figure 7. Effect of time on viscosity of Hycar 2106/Prepolymer C adhesive

ever, the solvent used has to be reasonably dry due to the reactive nature of the isocyanate prepolymer with water. The viscosity of the PSA system in the different solvents may not be the same due to the difference in the initial solvent viscosity and the solubility of the polymers.

In summary, BFG has developed a series of new reactive acrylic liquid polymers for the PSA industry. The PSA converters can process BFG 30% solids system with their existing equipment without modification and obtain superior PSA properties, such as excellent static shear (at R.T. and 70°C) and rolling ball tack, good peel strength and low vinyl film shrinkage. They will also be able to conform to the more stringent requirements of reducing energy consumption and meeting EPA emission standards with only very minimum capital outlay.

Abstract

Energy consumption and EPA standards are becoming important considerations to pressure sensitive adhesive (PSA) converters. The BFGoodrich Hycar® 2100R series of polymers is a new product concept designed to fulfill the changing needs of the PSA industry. These polymers are designed specifically to conform to those more stringent requirements while maintaining superior performance properties and minimizing equipment additions or modifications. The Hycar 2100R products are reactive acrylic liquid polymers and are furnished as 70% solids solutions which when combined with Isocyanate Prepolymer C and catalyst give a PSA formulation of approximately 80% solids. This high solids system is compatible with conventional coating equipment such as knife-over-roll and reverse roll. A 90% solids Hycar 2106-based PSA system has been successfully processed by a reverse roll coater incorporated with a Twinflo metering-mixing equipment. This paper covers: (1) the economic advantages of this high solids system due to reduced solvent requirements and reduced energy needs to evaporate solvents, when compared with conventional acrylic solution polymer PSA systems; (2) the PSA properties attained including a combination of excellent static shear and rolling ball tack, good peel strength, and excellent vinyl film shrinkage resistance; (3) the property changes that occur by varying the ratio of Hycar 2100R polymer to isocyanate prepolymer resulting in a family of products; and (4) the processing parameters.

References

(1) R. G. Marchessault and A. P. Plummer, Adhesive Age, 20, No. 4, April, 1977, p. 34.

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10

Energy Conservation in Cotton Ginning

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Cotton ginning is the first process in a long chain of processing and manufacturing operations required to convert raw seed cotton into usable consumer products. Although the primary function of cotton ginning is separation of cotton fibers from cottonseed, the modern ginning process also includes seed cotton drying and cleaning, lint cleaning, and bale packaging. The various ginning operations are connected by an intricate materials-handling system that forms a continuous flow process from seed cotton input to bale output. In the United States about 2,900 cotton gins process our annual 10- to 12-million bale cotton crop (1).

A gin's materials-handling equipment and its cleaning and ginning machinery are normally powered by induction-type, squirrel-cage electric motors. Heat for the seed cotton drying process is obtained by burning natural or liquefied petroleum gas in direct-fired burners in pneumatic conveying lines. The amount of energy consumed by the ginning process varies over a wide range due to differences in size and design, to fluctuations in the moisture and foreign matter content of cotton, and to variations in operating procedures. The energy consumption values given in Table I are representative of moderate-size plants that gin machine-picked cotton under optimum conditions. No allowances were made in Table I for energy consumed during idling or other nonproductive periods. Excessive idling or underutilization of ginning capacity will produce appreciably higher energy consumption values (2, 3) than those obtained under optimum conditions.

Of the 177 kwh of fossil fuel equivalent energy consumed in ginning a bale of cotton, 89 kwh, or 50% of the total, is required for seed cotton drying (Table I). This consumption value includes electric energy for the operation of air-moving fans and equivalent of 66 kwh (225,000 Btu) of energy for heating the drying air. The materials-handling operations, which are mostly pneumatic, consume the second largest amount of energy in a cotton gin. The gin's pneumatic conveying systems consume

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Table I. Representative Energy Requirements Per Bale, for Ginning Cotton.[a,b]

Ginning function	Energy requirements		Fossil fuel equivalents[c]	
	Electric energy, kwh	Drier fuel,[d] 1,000 Btu	Consumption, kwh	Distribution, %
Cleaning	5	---	15	9
Drying	8	225	89	50
Ginning	7	---	20	11
Packaging	3	---	9	5
Materials handling	15	---	44	25
Total	38	225	177	100

[a] Energy requirements were based on a fully utilized model gin that processes machine-picked cotton at rates of 12 to 14 bales/hr and do not include energy consumed during idling or other periods of downtime.

[b] Energy requirements derived from Tables A-17 and A-21 of reference (4) and Table 3 of reference (5).

[c] The calculation of fossil fuel equivalents for electric energy was based on a generation efficiency of 34% (10,000 Btu of fossil fuel energy required to generate 1 kwh of electricity.)

[d] Fuel requirements for driers are variable. They range from zero for dry cotton to as much as 450,000 Btu/bale for wet cotton.

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about 44 kwh of energy/bale, which represents 25% of the gin's total energy consumption. Lesser amounts of energy are consumed by the other ginning operations. The lint-seed separation, seed cotton and lint cleaning, and bale packaging operations account for 11, 9, and 5 percent, respectively, of the gin's energy requirements.

The seed cotton drying operation, because of its high energy consumption in relation to that of other ginning operations appears to be the most likely candidate for energy conservation in a cotton gin. The recognition of this potential has resulted in the development and identification of several applicable energy conserving techniques. The purpose of this paper is to describe some of the most promising techniques for conserving energy at cotton gins.

Energy Conservation Techniques

Drying Requirements. The amount of energy consumed during seed cotton drying varies directly with drying temperature. It is important to control drying temperature accurately, not only to insure satisfactory drying, but also to avoid excessive drying, which wastes energy and lowers fiber quality. The amount of heat required to achieve satisfactory drying depends upon the fiber's initial moisture content and the optimum final moisture content to which the fiber should be dried. Since a ginner has little control over initial fiber moisture content, it is important that we identify the "optimum moisture content" to establish a rational basis for drying decisions.

Past research on seed cotton drying has established an optimum range of fiber moisture content within which satisfactory cleaning and ginning can be achieved while the inherent qualities of the fibers are maintained (6, 7, 8). The currently accepted optimum fiber moisture content lies within the 6% to 8% (wet basis) range. This optimum range is a compromise between effective cleaning and quality preservation on the one hand, and quality preservation and smooth ginning on the other. Cotton that contains moisture in excess of 8% will not clean and gin properly and will receive low grades due to excessive trash and rough preparation (7). Cotton having moisture contents below the optimum range is subject to excessive fiber breakage during ginning (8), and the low moisture contents contribute to the generation of static electricity, causing chokages and decreased operating efficiency (9).

Information in Table II describes the performance characteristics of typical seed cotton drying systems and illustrates some of the effects of drying fibers to a level below the optimum. Generally, these data show that fibers ginned at moisture contents below 6 percent were shorter and produced lower yarn break factors than fibers ginned at moisture contents above 6%. Obviously, the amount of energy required for drying

Table II. Some Effects of Seed Cotton Drying on Fiber and Yarn Properties.[a]

Amount of seed cotton drying	Fiber properties Moisture contents, %[b]	Nonlint content %	Mean length, in.	Yarn properties Break factor units	Appearance index
7% to 8% initial fiber moisture content					
2 stages, amb.[c]	6.3	2.3	0.93	1903	96
2 stages, 150°F	4.8	2.1	0.91	1800	94
2 stages, 200°F	4.2	2.0	0.88	1737	90
8% to 9% initial fiber moisture content					
2 stages, amb.[c]	7.0	3.1	1.03	2004	93
2 stages, 180°F	5.1	2.5	0.99	1828	103
2 stages, 275°F	4.9	2.3	0.98	1781	100
9% to 10% initial fiber moisture content					
2 stages, amb.[c]	9.0	8.6	0.98	1686	79
1 stage, 250°F	6.7	7.3	0.95	1658	79
2 stages, 250°F	4.9	6.4	0.92	1585	76

[a] Data from references (6), (10), and (11).

[b] At the gin stand.

[c] Ambient air at about 70°F.

to low moisture levels is considerably greater than that required to achieve the 6% to 8% moisture range. Drying to levels below 6% tended to enhance trash removal, but this advantage was small and research has shown that it is often negated as a result of decreases in staple length and bale weight (6).

Thus, the first tenet in an energy conservation program for seed cotton drying may be simply stated as "use only the amount of drying required to lower fiber moisture content to the 6% to 8% range." Although this concept may sound elementary and obvious, it is surprising how often it is ignored.

Management of Drying Systems. The management of seed cotton drying systems to minimize fuel usage has not been an overriding consideration in the past because of relatively low fuel prices. However, with increasing fuel costs and the continual possibility of fuel curtailment, a critical evaluation of alternatives available to managers to reduce fuel consumption is of increased importance.

A typical seed cotton drying system is composed of two centrifugal fans, a burner, a tower drier, and connecting air lines (Figure 1). The first fan, called a push fan, takes ambient air from the gin room and discharges it through the burner and conveying lines to the tower drier. Seed cotton is dropped into the heated air stream between the burner and tower drier. The hot conveying air transports the seed cotton through serpentine passageways in the tower drier and delivers it to an air-fed cleaner or separator, while the hot air is routed to the second centrifugal fan (pull fan). The push-pull fan arrangement is necessary to overcome the airflow resistance of the tower drier and air lines. A typical gin is usually equipped with two drying systems of this type, which we commonly refer to as a two-stage drying system.

Because of the fixed nature of current drying systems, a gin manager's control of the system is limited to temperature regulation. The manager has little control over initial moisture content, ambient relative humidity, or the amount of equipment used. There is little likelihood that a manager will ever have an appreciable amount of control over initial moisture content, but with minor modifications to the drying system, he can exercise greater control of equipment usage and can often take advantage of low ambient humidity conditions to reduce fuel consumption.

During periods of low relative humidity, cotton often arrives at a gin with a fiber moisture content within or slightly below the optimum moisture range. Under these conditions seed cotton drying is not required and a considerable amount of fuel can be saved by turning off the burners. However, in most gins it is still necessary to route seed cotton through the tower driers. In these instances a tower bypass (Figure 1) can be used to further reduce energy consumption. The airflow resistance

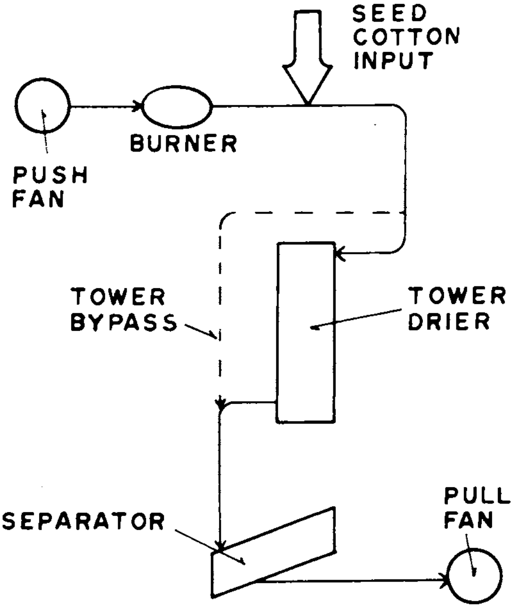

Figure 1. Flow diagram of a typical single-stage, seed cotton drying system equipped with a tower bypass

of the drying system is greatly diminished by bypassing the tower drier--so much so that one of the centrifugal fans can be eliminated. Therefore, in a gin having a two-stage drying system two fans can be eliminated, thereby saving about 12 kwh/bale (Table III).

Table III. Energy Consumption of Air-Moving Fans In a Typical Two-Stage Seed Cotton Drying System, With and Without Bypasses.

Air-moving fan	Energy consumed (kwh/bales)[a] for typical two-state drying system with: Airflow through drying towers	Energy consumed (kwh/bales)[a] for typical two-state drying system with: Drying towers bypassed
Two push fans	12	0
Two pull fans	12	12
Total	24	12

[a] Kilowatt-hours of fossil fuel equivalents.

Close attention to equipment utilization and drier temperature can greatly reduce energy consumption during seed cotton drying. Although the amount of flexibility available to a manager will depend upon operating conditions and equipment design, a few of the many possibilities available are given in Table IV. The wide range in energy consumption rates for the various alternatives shown in this table indicates that careful management of a drying system can be a valuable conservation tool.

Insulated Drying Systems: Seed cotton drying systems are typically constructed of 16- to 22-gage uninsulated steel sheet. These systems, because of large surface areas and high thermal conductivities, lose large quantities of heat through the walls of the conveying conduits and tower driers. It is not uncommon for the drying air temperatures to drop 100° to 200°F while passing through the drying system (12). Until about 25 or 30 years ago, many drying systems at cotton gins were insulated, particularly those at which tower driers were outside the gin building. Over the years outside drying installations were gradually relocated to the inside of gin buildings, and insulated systems lost their appeal. Also, with low fuel prices there was little financial incentive for insulating drying systems. However, recent increases in fuel prices and the increased possibility of fuel curtailment during the ginning season have prompted a re-evaluation of these systems.

Studies have recently been completed in which an insulated seed cotton drying system was compared with an identical

Table IV. Alternative Equipment Arrangements for Various Seed Cotton Drying Requirements and Ambient Relative Humidities.

Drying Needs[a]	Ambient humidity range	Equipment arrangement: No. 1 burner output	No. 1 drier usage	No. 2 burner output	No. 2 drier usage	Energy consumption range,[b] kwh/bale
High	All	High	Use	High	Use	110-150
Moderate	Medium to high	Medium	Use	Medium	Use	65-110
	Low	High	Use	Off	Bypass	60-80
Low	High	Low	Use	Low	Use	45-65
	Medium	Low	Use	Off	Bypass	30-40
	Low	Off	Use	Off	Use	20-30
None	High	Off	Bypass	Low[c]	Use	30-40
	Medium to low	Off	Bypass	Off	Bypass	10-15

[a] Qualitative description of the amount of drying needed to lower fiber moisture content to the optimum range or to maintain moisture content within the optimum range.

[b] Estimated per-bale energy consumed is expressed in kwh of fossil fuel equivalents.

[c] Fibers within or slightly below the optimum moisture range may require some heat to maintain these moisture levels when ginning under high relative humidity conditions.

ininsulated system (13). Each drying system consisted of a direct-fired burner, a push-pull fan system, a 24-shelf tower drier, and about 90 lin ft of conveying line. For the insulated system, all conveying lines were covered with 1-in-thick fiber glass batt, and the tower was covered with 1-in-thick, rigid fiber glass board. The thermal conductance of the fiber glass insulation equaled 0.25 Btu/hr/ft^2/°F and the insulation was rated for a maximum operating temperature of 450°F. Drying air temperatures were monitored at the burner outlet, cotton mixpoint, and tower outlet while processing seed cotton at a rate of 8 bales/hr. Drying response was determined from moisture samples taken before and after drying. Appropriate data from these studies are summarized in Tables V and VI.

Table V. Drying Temperatures and Performance Characteristics of Insulated and Uninsulated Single-Stage Drying Systems.[a]

Type of system	Air temperature (°F) at: Burner outlet	Cotton mixpoint	Tower outlet	Temperature drop, °F [b]	Drying response gr/lb [c]
Insulated[d]	350	300	160	140	120
Uninsulated	350	281	122	159	92

[a] The drying systems were operated at a seed cotton drying rate of 8 bales/hr.

[b] Difference in temperature between cotton mixpoint and tower outlet.

[c] Amount of moisture removed from seed cotton with an initial moisture content of 8.6%, in grains/lb of seed cotton.

[d] One-inch-thick fiber glass insulation, k=0.25 Btu/hr/ft^2/°F.

At equal burner outlet temperatures, the insulated system operated at higher drying air temperatures than the uninsulated system, both at the cotton mixpoint and tower outlet (Table V). At a 350°F burner temperature, the temperature drop from mixpoint to tower outlet averaged 140°F for the insulated system and 159°F for the uninsulated system. These temperature drops were due not only to losses of heat from the drying systems, but also, in part, to heating the cotton. The insulated system removed 120 grains of moisture per pound of cotton (gr/lb), whereas the uninsulated system removed only 92 gr/lb—indicating an increase in drying efficiency due to insulation.

Drying response data were obtained for each system over a range of operating temperatures to estimate energy savings. At equal levels of drying, the insulated system operated at lower temperatures and consumed less energy than did the uninsulated system (Table VI). The saving in energy required to heat drying air ranged from 20.6% to 26.9%, depending on operating temperature and drying level. Since the energy saving tended to decrease with increases in operating temperature, it appeared that thick insulation would be advantageous for the high temperatures.

Table VI. Effect of Insulation on Operating Temperatures and Energy Consumption of a Single-Stage Drying System.[a]

Level of drying and type of system[b]	Burner outlet temp., °F	Cotton mixpoint temp., °F	Energy consumption[c] kwh/bale	Energy savings[d] %
70 gr/lb:				
Insulated	211	192	29.3	26.9
Uninsulated	274	238	40.1	----
88 gr/lb:				
Insulated	260	230	37.7	26.0
Uninsulated	337	271	50.9	----
105 gr/lb:				
Insulated	310	268	46.3	20.9
Uninsulated	381	304	58.5	----

[a] Seed cotton drying rate of 8 bales/hr.

[b] Level of drying in grains of moisture removed/lb of seed cotton.

[c] Theoretical energy required to heat ambient air to burner outlet temperature.

[d] The percentage of reduction in energy consumption for heating gained through use of insulation.

An energy saving of the magnitude experienced in this study would represent a cost saving of 10 to 15 cents/bale for ginners who insulate two drying systems. At an estimated installed cost of $1,500, gins could recover their investment after ginning 10,000 to 15,000 bales of cotton. Most gins could achieve these break-even volumes in about 1 to 3 years.

Heat Recovery Devices: The heated air used for seed cotton drying is normally exhausted to the atmosphere after one pass through a tower drier. Since the exhaust air is still relatively warm (100°-200°F), this practice wastes about 10% to 20% of the thermal energy used for drying (14). Unfortunately, direct reuse of the exhaust air is complicated by the need to clean the air before it is reheated in direct-fired burners. During drying and the subsequent seed cotton separation process, drying air becomes contaminated with leaf trash, fly lint, and dust. Additional air cleaning devices and more elaborate conduit arrangements increase the complexity and cost of recirculating systems. Nevertheless, experimental recirculating systems have been successfully demonstrated (15), but these systems have not gained commercial acceptance.

Another possibility for recovering heat from exhaust air involves the use of a heat exchanger in the exhaust line. A heat exchanger can be used to transfer some of the heat from the dirty exhaust air to fresh air entering the burner. This transfer process raises the temperature of the fresh air and reduces the heating load on the burner. Potential fuel savings resulting from use of heat exchangers depend upon the efficiency of the heat transfer process and the amount of recoverable energy available in the exhaust air (Table VII). Childers (14) reported that a fuel saving of 3% to 6% was gained when a heat exchanger was used on the exhausts of uninsulated and insulated drying systems. In that study actual heat exchanger efficiencies ranged from 18% to 27%. McCaskill (16) reported an efficiency of about 31% for a special cyclone-type heat exchanger used in high-temperature applications. Also, commercial heat-pipe exchangers are frequently rated as high as 50% efficient. Thus, depending on heat exchanger efficiency and temperature of exhaust air, a fuel saving of 3% to 10% appears possible.

Table VII. Potential Fuel Savings for Insulated and Uninsulated Drying Systems at Various Operating Efficiencies of Heat Exchangers.

Type of system	Energy available from exhaust air,%[a]	Potential fuel savings (%) at heat exchanger efficiencies of:			
		20%	30%	40%	50%
Insulated	20	4.0	6.0	8.0	10.0
Uninsulated	15	3.0	4.5	6.0	7.5

[a] Percentage of total heating requirements for drying that is available in exhaust air from representative drying systems.

Utilization of Ginning Waste

If waste byproducts from the cotton ginning operation are not utilized in some manner, they create a disposal problem. Conversely, ginning waste is an excellent source of raw material that can be converted into energy, on-site, and utilized concurrently during the processing operation. Research has shown that the heat value of cotton gin waste averaged 7,928 Btu/lb (dry weight) or about 7,000 Btu/lb at 11% moisture content (17).

Several heat-recovering incineration systems are being evaluated at cotton gins across the nation (18). One of these systems, installed in 1973 at the U.S. Cotton Ginning Research Laboratory, Stoneville, Mississippi, is shown schematically in Fig. 2. This system is composed of a continuous trash feeder, two burning chambers, a heat exchanger in the stack, a modulating hot-air mixing valve, and a conventional gin-drying system (16).

The trash feed system consists of a high-efficiency cyclone that is equipped with a vacuum feeder that discharges into a screw conveyor. As the waste moved progressively through the lower chamber due to the additional charges of trash, it is reduced to ash and discharged from the incinerator by the automatic ash removal cylinder.

The incinerator has operated on the controlled-air principle with minimum excess air. The lower chamber of the incinerator is equipped with two natural gas burners to ignite the trash and help preheat the chamber during initial startups. Those burners can be completely turned off when preheating has been accomplished. The upper chamber is equipped with one burner to insure ignition of the smoke in the upper chamber. This burner is automatically turned off by a controller at about 1,400°F. Ignition is self-sustaining above this temperature.

A vane-axial fan was installed at the inlet to the heat exchanger to insure positive pressure of the ambient air in the heat exchanger, to overcome the static-pressure loss caused by the heat exchanger and to insure continuous flow of ambient air through the heat exchanger to prevent damage by excess heating. The ambient air moved in a cyclone path through the heat exchanger as indicated in Fig. 3. Spiral fins in the stack gas chamber and inner ambient air chamber improve the heat transfer process by increasing the exposed surface area and by extending the dwell time of stack gas and ambient air.

The control system is composed of a modulating mixing valve, a conventional gin-type gas burner, and a conventional gin-type temperature controller. The heated air delivered from the heat exchanger enters a specially designed, modulating hot-air mixing valve (Fig. 2). This valve is controlled by the gin's drying system controller and is capable of discharging heated air to the atmosphere, of directing it to the gin's drying system, or of mixing it with ambient air in the desired proportion and directing

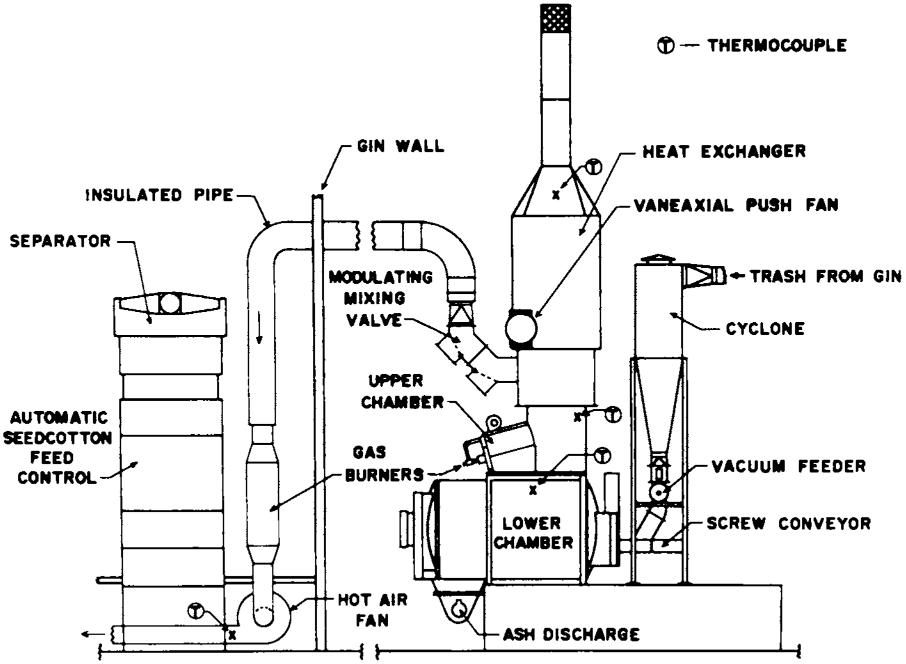

Figure 2. Schematic of heat-recovery incineration system

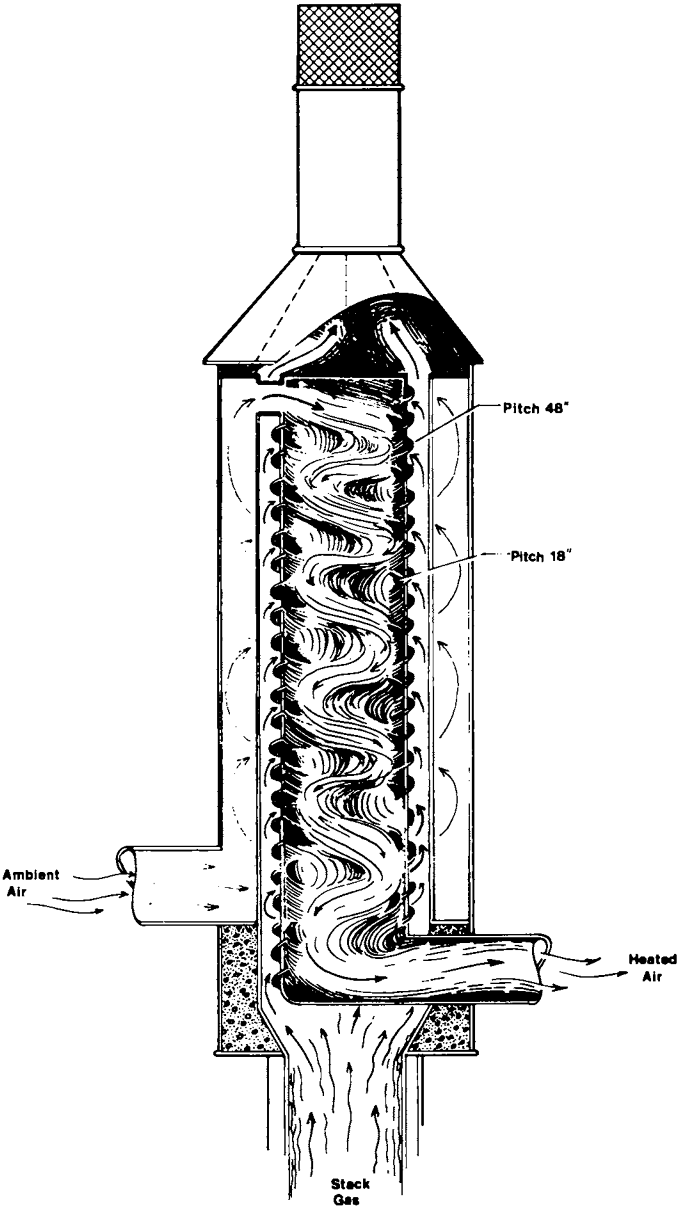

Figure 3. Cutaway of heat exchanger designed by U.S. Cotton Ginning Research Laboratory

it to the gin's drying system.

The conventional gas burner was connected in series with the heat exchanger (Fig. 2). The gas burner then could assist with initial startup and could supplement the heat exchanger if it became necessary. Both the modulating valve and the gas burner were regulated by the same temperature controller. The incinerator heat exchanger was the primary heat source, and the gas burner was the secondary source. The control system automatically turns off the gas burner when the incinerator heat is sufficient to satisfy the demand.

The average temperatures in the heat-recovery system are shown in Table VIII. The average air volume delivered to the cotton mixpoint was 6,630 std ft^3/min. The heat recovered by the heat exchanger and delivered to the feed control was almost one million Btu/hr from the burning of only 450 lb of waste/hr. The overall system recovery efficiency was almost 31%. Data relative to the available heat and the heat recovered are as follows:

Available heat from combustion (450 lb/hr)	3,150,000 Btu/hr
Recovered heat at cotton mixpoint (309°F)	1,759,000 Btu/hr
Available heat from ambient air (91°F)	794,000 Btu/hr
System's recovered heat	965,000 Btu/hr
System efficiency	30.63%

Table VIII. Temperatures in Heat-Recovery system.[a]

Description	High	Low	Average
Stack gas at			
Heat exchanger inlet, °F	2,357	2,116	2,251
Heat exchanger outlet, °F	795	620	701
Heated air at			
Heat exchanger inlet, °F	94	88	91
Heat exchanger outlet, °F	376	277	337
Cotton Mixpoint, °F	318	261	302

[a] Average for 3 hr of burning at a trash feed rate of 450 lb/hr. Temperatures were recorded at 1-min intervals.

The successful operation of this system demonstrated the potential for heat recovery from incineration of cotton gin trash. At a 30% recovery ratio, enough heat can be recovered from the incineration process to supply most of the energy required for seed cotton drying, even in low-capacity gins (Table IX). Only the size and volume of the ginning operation will dictate whether such recovery will be economically feasible.

Table IX. Potential for Heat Recovery from Incineration of Gin Trash.

Processing rate, bales/hr	Heat from combustion,[a] million Btu/hr	30% heat recovery for drying, million Btu/hr
6	8.4	2.5
8	11.2	3.4
10	14.0	4.2
12	16.8	5.0
15	21.0	6.3
20	28.0	8.4
25	35.0	10.5
30	42.0	12.6

[a] Based on 200 lb of trash/bale, with a heat value of 7,000 Btu/lb.

Summary and Conclusions

Many opportunities exist for energy conservation in the ginning of cotton, particularly for seed cotton drying--a process that accounts for a large percentage of the energy consumed at modern cotton gins. Several energy conservating techniques applicable to the drying process have been identified and are available to the ginning industry.

Improved control of the drying process through close management would eliminate the problem of overdrying, which wastes energy and lowers fiber quality. Ginners can also reduce energy consumption by taking advantage of low relative-humidity conditions that exist periodically in many areas of the cotton belt. Under such conditions, unheated ambient air has considerable drying potential. Some cotton arrives at the gin with a moisture content within the optimum range for ginning, and such cotton requires no additional drying. The tower driers can be bypassed in these situations. Such bypassing would result in substantial savings in electric energy.

Drying efficiency can be improved by reducing heat losses from the drying system. Relatively inexpensive insulation on conveying lines and tower driers can reduce fuel consumption as much as 27%. Fuel savings could also be realized by recovering waste heat from the exhausts of drying systems. Heat exchangers in drying system exhaust lines can reduce fuel consumption by 3% to 10%, depending on heat exchanger efficiency.

Ginning waste is a valuable source of energy for cotton gins. Each pound of gin waste has a heat value of about 7,000 Btu. A 30% recovery of heat from the incineration of gin waste is sufficient to provide most of the heat required for seed cotton drying.

The energy conserving techniques described in this paper are technically feasible, but economic feasibility often depends on gin size and annual volume. Although all of the techniques described may not be applicable to all gins, most gins could effectively use one or more of the techniques to reduce fuel consumption and processing costs.

Literature Cited

1. USDA, Cotton Gin Equipment, USDA, Agr. Market Serv. Cotton Div. Rpt. (1977), 3.
2. Fuller, S. and Washburn, M., Factors Affecting Consumption and Cost of Energy Utilized in the Cotton Ginning Process, presented at Symposium on Managing Energy Wisely in Cotton Gins at Lubbock, Texas, October 3, 1977, 12.
3. Wilmont, C. A. and Watson, H., Power Requirements and Costs for High-Capacity Cotton Gins, USDA Market Res. Rpt. No. MRR 763 (1966), 23.
4. Shaw, D. L., Cleveland, O. A., and Ghetti, J. L., Economic Models for Cotton Ginning, USDA, Econ. Res. Serv., Texas Tech Univ. Pub. No. T-1-158 (1977), 60.
5. Willcutt, H., Effects of Feeding Systems on Gin Output and Energy Consumption, The Cotton Gin and Oil Mill Press (1976) 77 (18), 14-16.
6. Childers, R. E., and Baker, R. V., Effect of Moisture Conditioning on Ginning Performance and Fiber Quality of High Plains Cotton, Trans. ASAE (1978), 21 (2), 379-384.
7. Leonard, C. G., Ross, J. E., and Mullikin, R. A., Moisture Conditioning of Seed Cotton in Ginning as Related to Fiber Quality and Spinning Performance, USDA Market Res. Rpt. (1970) No. MRR 859, 16.
8. Moore, V. P. and Griffin, A. C., The Relationship of Moisture to Cotton Quality Preservation at Gins, USDA-ARS (1964), ARS 42-105, 11.
9. Leonard, C. G., Controlling Static Electricity on Cotton During Ginning With an Antistatic Agent, USDA Agr. Res. Serv. Rpt. (1960), ARS 42-39, 16.
10. Cocke, J. B., Kirk, I. W., and Wesley, R. A., Spinning Performance and Yarn Quality as Influenced by Harvesting, Ginning, and Mill-Processing Methods, USDA Market Res. Rpt. (1977), No. MRR 1066, 25.
11. Mangialardi, G. J. and Griffin, A. C., Moisture Restoration to Cotton at the Gin: Effects on Fiber and Spinning Properties, USDA Market Res. Rpt. (1965), No. MRR 708, 10.
12. Cocke, J. B., Effects of Input Temperature and Air Volume on Moisture Removal from Seed Cotton, USDA Agr. Res. Serv. Rpt. (1975), ARS-S-67, 8.

13. Childers, R. E., Insulated Drying System: Key to Conserving Fuel, Cotton Ginners' Journal and Yearbook (1978), 46 (1), 6-9.
14. Childers, R. E., Heat Recovery Systems for Cotton Gin Driers, presented at Southwest Regional Meeting ASAE, February 5-8, 1978.
15. Leonard, C. G. and Gillum, M. N., The Monoflow Air System for Cotton Ginning, The Cotton Gin and Oil Mill Press (1968), 69 (11), 10,11 and 23,24.
16. McCaskill, O. L. and Wesley, R. A., Energy From Cotton Gin Waste, Cotton Ginners' Journal and Yearbook (1976), 44 (1), 5-14.
17. Griffin, A. C., Fuel Value and Ash Content of Ginning Waste, Trans. ASAE (1976), 19 (1), 156-158, 167.
18. Lalor, W. F., Jones, J. K., and Slater, G. A., Test Results from Waste-Fired Gin Dryers, Cotton Inc., Agro-Industrial Rpt. (1977), 3 (7), 1-16.

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11

Sizing and Desizing Textiles with Degraded Starch and Ultrasonic Techniques to Conserve Energy

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The main purpose of applying sizing agents to warp yarns is to add tensile strength and resistance to abrasion. These two yarn qualities are vital for preventing yarn deterioration and breakage during loom weaving. After being woven, the fabric ordinarily has to be desized, because the sizing agent impedes textile finishing such as dyeing or permanent press treatment. With conventional starch, hot water must be used in desizing. If degraded starches are used, however, the desizing can be done with ambient temperature water and ultrasonic accelerated techniques that result in an energy saving and high speed process.

Starch Degradation by Bacteria and Enzymes

Starch consists of two polymers, approximately 20% amylose and approximately 80% amylopectin (1, 2, 3). Both of these polymers are made up of D-glucose rings (Figure 1). Fermentation of starch by bacteria and its degradation by enzymes depolymerize the amylose and amylopectin into low molecular weight glucose polymers that are more soluble in water. This degradation is depicted schematically in Figure 2. By thin layer chromatography, gas-liquid chromatography, and titration, it was determined that a sizing solution that originally had 12% starch contained 11.5% degraded starch and 0.2% butyric acid after fermentation. No simple glucose or other sugars were detected. The mass balance evolved as CO_2, ethanol, and traces of other compounds such as proteins from the bacteria. The reaction may be represented approximately as follows:

$$(C_6H_{10}O_5)_n \rightarrow \text{(Degraded starches)} + C_4H_8O_2$$
$$+ C_2H_5OH + CO_2 + H_2O$$

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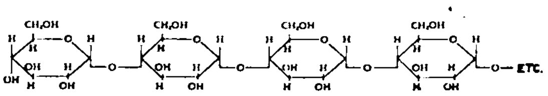
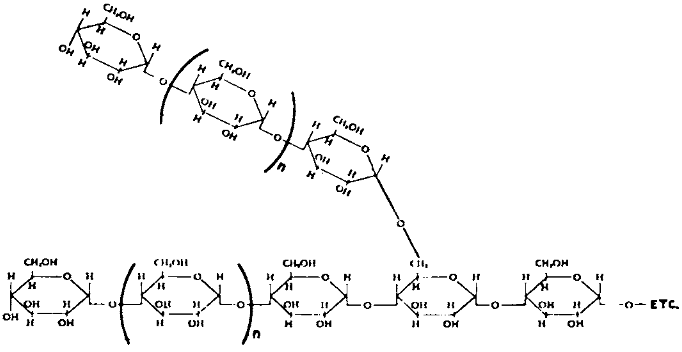
* Names of companies or commercial products are given solely for the purpose of providing specific information; their mention does not imply recommendation or endorsement by the U.S. Department of Agriculture over others not mentioned.

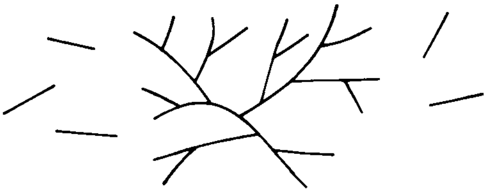


AMYLOSE



AMYLOPECTIN

Figure 1. Major chemical constituents of starch



AMYLOSE AND AMYLOPECTIN SCHEMATIC

DEGRADED STARCH SCHEMATIC

Figure 2. Schematic of amylose and amylopectin polymeric structure before and after degradation by bacteria or enzymes

Similar results are obtained with degradation by enzymes, but the entire 12% of the starch is converted to degraded amylose and amylopectin. The exact equations for these reactions are not known.

Iodine test of the fermented starch indicated a purple color, indicating the presence of chain lengths in excess of 40 glucose units. However, an iodine test of the enzyme-degraded starch initially produced a brown color, indicating the presence of less than 40 glucose units. But as the reaction progressed, a purple color dominated, verifying also the presence of chain lengths in excess of 40 glucose units (3).

Starch Solution Preparation

On a laboratory scale, starch solutions of 200 to 1,000 ml were prepared as follows: to a batch of ambient temperature water (New Orleans city water), 12% starch by weight was added and stirred until the mixture was uniform. The starch used was Crown thin boiling starch (manufactured by Penick & Ford). Lower grade starches may be used to achieve the fermentation at a lower cost. This starch mixture was heated to 95°C while stirring. The stirring was continued while the mixture was kept at 90-100°C for 1 hr. This is the conventional means of sizing solution preparation, and the size must be used while hot, otherwise a gel is formed upon cooling (Table I).

A second starch solution was prepared as above, poured into a jar, allowed to cool, and loosely covered to allow venting of gases during fermentation. This jar was kept at ambient temperature and stirred once a day with a spatula. Aeration is important because the process is aerobic. Measurement of pH is a good means of determining the progress of fermentation; bacteria action on the degradation of starch is diminished when the pH drops to approximately 3.5 within about 2 weeks (Figure 3).

A third starch solution was prepared as above, and, while hot, an enzyme was added (1.5% of the starch weight) and mixed thoroughly. The mixture was allowed to cool to ambient temperature, and the starch degradation was completed within 4 hours. The enzyme used was commercial product Rhozyme GC Extra.

A pilot plant scale starch solution, approximately 300 l, was prepared in a stainless steel container equipped with a paddle wheel electric stirrer, steam-heated coils, steam injection, an external gear pump with recirculation capability, insulation surrounding the container, a container lid, and a vent. The starch solution was prepared with the same percentage composition and duration of heating as described for the laboratory scale process. The first batch was pumped into the "sizing box" of the slasher and utilized immediately hot as a conventional yarn treatment.

The second batch of starch solution, approximately 300 l, was prepared as above, and at the end of 1 hr of heating, the

Table I. Starch Size Preparation (12% by Weight Aqueous Starch Solution)

TYPE OF SIZE	PROCESS
CONVENTIONAL HOT STARCH	HEAT SOLUTION AT 95°C FOR ONE HOUR AND APPLY TO YARN HOT
STARCH FERMENTED	HEAT SOLUTION AT 95°C FOR 5 MINUTES ALLOW AEROBIC FERMENTATION, MIX THOROUGHLY ONCE A DAY, READY FOR USE IN TWO WEEKS.
STARCH ENZYME	HEAT SOLUTION AT 95°C FOR 5 MINUTES ADD 1.5% ENZYME ON WEIGHT OF STARCH WHILE HOT AND MIX THOROUGHLY, READY FOR USE IN 4 HOURS.

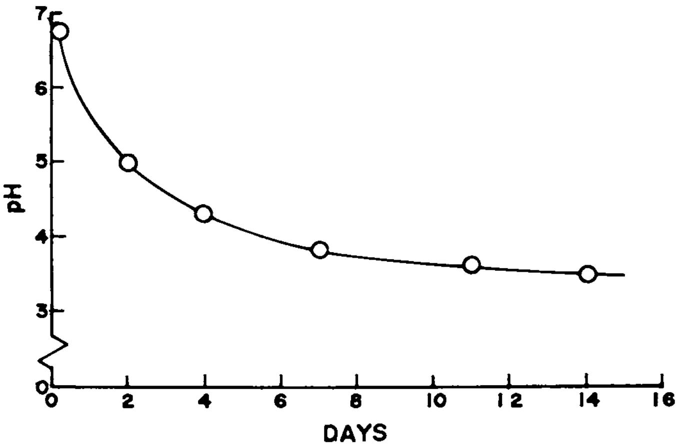


Figure 3. Change in pH of fermented starch as a function of time

In Energy Conservation in Textile and Polymer Processing; Vigo, T., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 1979.

tank lid was closed and allowed to stand. Once a day the lid was opened and the stirrer turned on to aerate and mix the starch. The pH was measured at approximately 2-day intervals. The solution was ready to be applied to yarn after 14 days (Figure 3). Just prior to the application of the fermented starch to the yarn, the paddle wheel was turned on for stirring and the gear pump turned on for recirculation. Both were run for 1 hr to achieve a uniform fluid mixture.

Currently, research is in progress to increase the fermentation rate so that the starch solution will be ready for use within 3 days instead of 14 days.

The third batch of starch solution, approximately 300 l, was prepared as above, and at the end of 1 hr of heating, the enzyme was added (1.5% of the starch weight) and mixed thoroughly. The solution was allowed to react with the enzyme for at least 4 hours. Just prior to the application of the enzyme-degraded starch to the yarn, the paddle wheel was turned on for stirring and the gear pump turned on for recirculation. Both were run for 1 hr to achieve a uniform fluid mixture.

Comparison of Processes

A schematic of the conventional process for treating yarn with a sizing agent and the modified process (dotted lines) for conserving energy is shown in Figure 4.

Initially, the powdered starch must be thoroughly stirred in ambient temperature water until the mixture is uniform. The customary mixture is 12% by weight. The mixture is heated to approximately 95°C and stirred and cooked for 1 hr. This mixture is transferred to the slasher, where it is kept hot to prevent gel formation while being applied to the warp yarn.

In the modified process, heating the starch mixture to approximately 95°C for 5 minutes is sufficient. This mixture is stored from a few hours to 2 weeks, depending on the mode of starch degradation selected. Longer storage of the degraded starch is not detrimental, but prior to its use it has to be mixed to uniform fluidity and transferred to the slasher, where it can be applied to the warp yarn either at ambient or elevated temperatures (Table I).

After the yarn is woven into a fabric, the partially degraded sizing agent is washed off. A schematic of the conventional process for desizing and the modified process (dotted lines) for conserving energy is shown in Figure 5.

Customarily, the fabric sized with ordinary starch is soaked in an enzyme solution at 70°C and transferred to heated bins (70°C) for 15 minutes to 4 hours to convert the film of ordinary starch, which is insoluble, to water-soluble polymers of glucose. The fabric is washed with hot (70°C) water.

In the modified process, the water-soluble starch may be removed from the woven fabric by soaking in ambient temperature

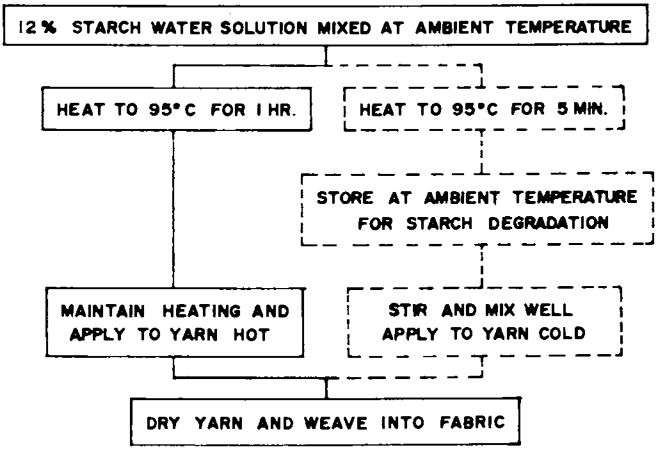


Figure 4. Comparison of processes for sizing yarns with conventional or degraded starch

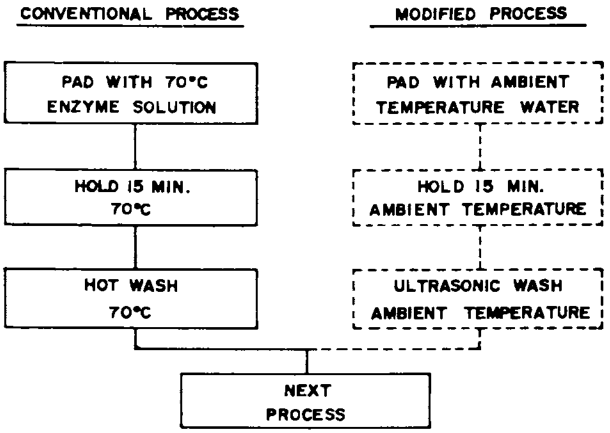


Figure 5. Comparison of processes for desizing fabrics sized with conventional or degraded starch

water, followed by size removal with ultrasonic accelerated techniques in an ambient temperature bath. In both processes, the fabric is then dried.

In summary, the major differences between the two processes are:

1. Reduced heating time during initial preparation of the starch.
2. Storage time for starch degradation.
3. Degraded starch is applied cold instead of hot.
4. Woven fabric is washed free of the starch in ambient temperature water augmented with ultrasonics, rather than soaking the fabric with an enzyme solution at 70°C, holding the fabric hot and washing in hot water.

For comparison of energy consumption, segments of fabrics were desized with both conventional hot water wash and ultrasonic desizing with ambient temperature water.

The methods employed for determining the energy consumptions involved test equipment. The monitoring of thermostatically controlled electric heater and the known specific heat of water and the fabric provided the data for conventional starch desizing process. The known duration and wattage of ultrasonic equipment provided data for ultrasonic desizing. The quantity of heat required to heat water for enzyme solution from 15 to 70°C was 767 W/kg water. To heat the fabric to 70°C was 230 W/kg; this was computed from specific heat of 1320 joules/kg°C. To sustain the temperature at 70°C required 400 W/kg fabric due to heat losses. For the final washing of the size from fabric required 1,000 W/kg fabric. Summing up, these energy consumptions yielded a total of approximately 2.4 kW/kg of fabric for desizing of fabrics sized with conventional starch. The measured energy consumed when desizing with degraded starches and ultrasonics was 0.5 kW/kg of fabric. Therefore, approximately a 75% reduction in energy consumption can be achieved by the modified process.

The total energy savings for the textile industry may be projected on the basis of a total annual consumption of 150 million kg (300 million lb) of corn starch and 1.5 billion kg (3 billion lb) of heated water. Energy savings could amount to approximately 2 billion kWh.

Yarn Test Procedures and Data

To obtain a quantitative measure of yarn weaving performance independently of a loom, the testing machines included the Uster automatic, Instron, and CSI Stoll flex abrader.

Initial test data on yarns sized with fermented and enzyme-degraded starches proved the inability of the sizing agent to add any strength to the yarn. The problem was solved by thoroughly mixing the degraded starch prior to application. The mixing step was necessary because the product of starch degradation is a three-phase mixture, i.e., solids, an aqueous solution, and gas bubbles.

The strength and elongation curves are presented in Figure 6. Comparatively, both degraded starches produced slightly better resilience and elongation characteristics in the lower stress levels of up to 200 g. In general, the elongation versus stress curves showed no significant difference in yarn performance characteristics.

Data from pilot plant tests for strength, elongation, and abrasion of cotton yarns treated with sizing agents are presented in Table II. Conventional starch was used as a standard of comparison. This conventional starch required hot application. The treatments appearing on the rest of Table II were applied at ambient conditions. Both the breaking strength and elongation properties of yarns, treated once with either fermented starch or enzyme-degraded starch, were equivalent to the conventional hot starch treatment. The breaking strengths were approximately 420 g, and the elongations were approximately 6.8%. Because the degraded starches were water soluble, it was anticipated that a second application after yarn drying would augment the properties. The breaking strengths did improve by about 10% but stiffness resulted. The elongation properties were therefore reduced proportionately.

The abrasion tests were performed with a Stoll flex abrader. The yarn was wound on a card, taped in a group, and cut to the dimensions indicated in Figure 7. The yarn treated with conventional starch exhibited significantly greater abrasion resistance qualities than the yarn treated with degraded starches. With ordinary starch, approximately 1,000 cycles of abrasion were required to break the yarn as compared to 400 to 600 cycles for the degraded starches. A significant improvement was observed by applying a second treatment which raised the number of cycles to a breaking point closer to that of ordinary starch. However, the question arose whether the higher degree of abrasion imparted by ordinary starch was necessary. This question remained to be answered in an actual weaving operation; the weaving results are presented in the following sections.

To determine the effect of the aging of degraded starch and the effect of drying temperature, a series of tests were run in which fermentation age was varied from 7 to 40 days and drying from 20°C to 100°C (Table III). The relatively small variations observed in the data indicated that neither aging nor temperature produced any significant effect on yarn properties.

In industrial scale operations, additives are used with sizing agents according to individual preference and the requirements for a particular situation. A brief study was made on two classes of additives: binding agents for dust abatement and lubricants for abrasion resistance. Five commercial lubricant additives were tried with fermented starch, and, of these five, two retained the breaking strength and elongation properties without degradation, while improving the abrasion properties by

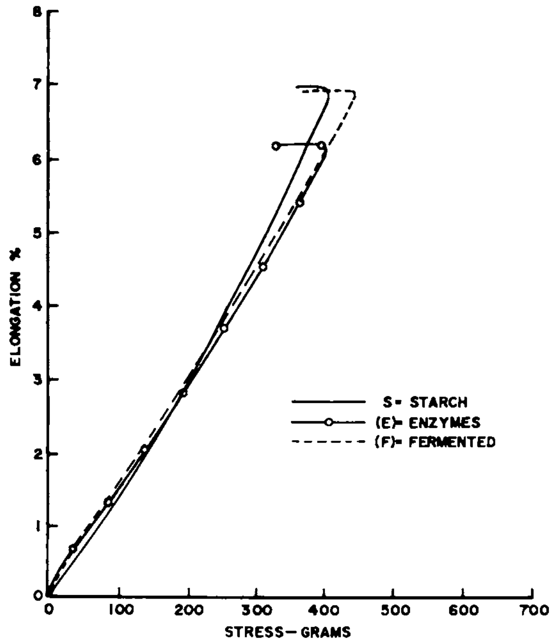


Figure 6. Elongation vs. stress of starch sized cotton yarn (33 mg/m)

Table II. Test of Cotton Yarn Treated with Sizing Agents (Yarn 33 mg/m)

TREATMENT	INSTRON		USTER		STOLL FLEX
	BREAKING STRENGTH (G)	ELONGATION (%)	BREAKING STRENGTH (G)	ELONGATION (%)	CYCLES TO BREAK
STARCH (CONVENTIONAL)	407	6.9	459	6.9	1007
STARCH FERMENTED	442	6.9	407	7.2	430
STARCH FERMENTED TWO TREATMENTS	519	5.66	496	6.4	848
STARCH ENZYME	417	6.18	406	6.8	618
STARCH ENZYME TWO TREATMENTS	499	4.63	510	5.8	661

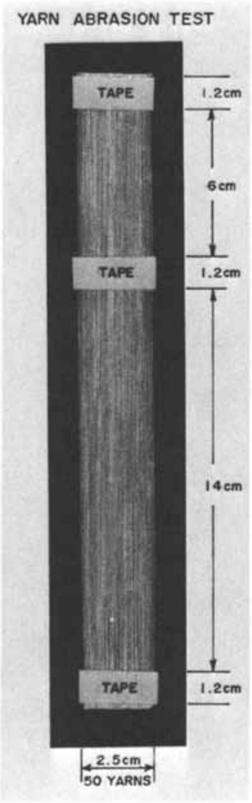


Figure 7. Method for determining abrasion resistance of yarns

approximately 10%. Table IV indicates this comparison of abrasion property improvement for additives B and C, compared to the other three.

A binding agent, 1% PVA (polyvinyl alcohol), was added to starch solution. This additive is often used for yarn blends of cotton and synthetics. As shown in Table IV, this additive improved breaking strength and elongation as well as abrasion properties.

The properties of a lubricant additive were combined with a binding agent by adding 1% lubricant B and 1% PVA (Table IV). The data indicated improvement in both strength and abrasion, but a slight reduction in elongation because of increased stiffness.

To determine whether degraded starches could be recovered in dry form and used at a later time, batches of fermented starches and enzyme-degraded starches were hot-air evaporation dried. Both produced crystalline solids that were redissolved in water in a 12% solution by weight and applied to yarn. Breaking strength, elongation, and abrasion were equivalent to the original degraded starches (Table V).

Weaving Tests on Experimentally Sized Yarns

To test the weavability of yarns treated with degraded starches, 20 mg/m carded cotton yarn was spun, and three types of size solutions were prepared in 300 l quantities as described above: ordinary starch, fermented starch, and enzyme-degraded starch. No additives were used in any of the size solutions. The size operation was done with a commercial slasher under normal operating conditions. The ordinary starch was applied hot at 90°C. The two degraded starches were applied to yarn at ambient temperatures; however, one notable exception was that for the enzyme-degraded starch where the pressure of the yarn squeeze rollers was cut to half of normal. This lower pressure was required because of the lower viscosity of the enzyme-degraded starch, which was approximately 2,000 mPas, as compared to 9,000 mPas for ordinary hot starch and 68,000 mPas for fermented starch. These viscosities were measured by a Brookfield model RVT.

The weaving of the yarn was conducted on a Draper model X-P loom operating at 160 picks per minute. A 115 g/m^2 (3.4 oz/yd^2) printcloth fabric was produced with approximately 68 ends by 70 picks. The statistical data accumulated during the weaving operation of the three types of yarn treatments are presented in Table VI. The average number of breaks per hour in warp yarn for starch, fermented starch, and enzyme-degraded starch was 1.62, 1.37, and 1.45, respectively.

The statistical evaluation of weaving test data indicated that the yarns treated with degraded starches performed as well as yarns treated with conventional hot size. The multiple comparison testing of the three population means indicated that

Table III. Test of Cotton Yarns Treated with Sizing Agents (Yarn 33 mg/m)

TREATMENT	INSTRON TESTER	
	BREAKING STRENGTH	ELONGATION
SEVEN DAYS FERMENTED 20°C DRY	419	7.33
SEVEN DAYS FERMENTED AND REHEATED 20°C DRY	424	6.64
SEVEN DAYS FERMENTED 60°C DRY	359	6.95
SEVEN DAYS FERMENTED AND 80°C DRY	369	7.40
SEVEN DAYS FERMENTED 100°C DRY	389	7.18
SEVEN DAYS FERMENTED, TWO PASSES 20°C DRY	441	6.70
SEVEN DAYS FERMENTED, TWO PASSES 100°C DRY	434	7.10
FORTY DAYS FERMENTED 20°C DRY	378	7.50

Table IV. Test of Cotton Yarn Treated with Sizing Agents and Additives (Yarn 33 mg/m)

TREATMENT	INSTRON		STOLL FLEX
	BREAKING STRENGTH (G)	ELONGATION (%)	CYCLES TO BREAK
STARCH (FERMENTED)	460	7.07	439
STARCH (F) PLUS 1% COMMERCIAL LUBRICANT A	417	5.95	348
STARCH (F) PLUS 1% COMMERCIAL LUBRICANT B	469	6.69	534
STARCH (F) PLUS 1% COMMERCIAL LUBRICANT C	430	6.45	506
STARCH (F) PLUS 1% COMMERCIAL LUBRICANT D	395	6.86	334
STARCH (F) PLUS 1% COMMERCIAL LUBRICANT E	397	7.38	426
STARCH (F) OF 11% STARCH PLUS 1% PVA	482	7.56	505
STARCH (F) OF 11% STARCH PLUS 1% PVA, PLUS 1% COMMERCIAL LUBRICANT B	492	5.60	565

Table V. Test of Cotton Yarn Treated with Recycled Sizing Agents (Yarn 33 mg/m)

TREATMENT	INSTRON		STOLL FLEX
	BREAKING STRENGTH (G)	ELONGATION (%)	CYCLES TO BREAK
STARCH (FERMENTED) RECYCLED	496	5.50	667
STARCH (ENZYME) RECYCLED	522	6.70	633

Table VI. Weaving Tests of Experimentally Sized Yarns (Yarn 20 mg/m)

		WARP BREAKS		
PICKS	METERS	STARCH	STARCH FERMENTED	STARCH ENZYME
50,400	20	1	6	21
100,800	40	3	5	8
151,200	60	13	16	7
201,600	80	11	15	9
252,000	100	9	7	6
302,400	120	19	5	9
352,800	140	7	6	3
403,200	160	5	6	3
453,600	180	3	2	5
504,000	200	14	4	5
BREAKS/LOOM-HR.		1.62	1.37	1.45
SIZE ADD-ON %		11.30	14.80	15.40

there was no statistically significant difference among the warp breaks per hour for the three sizing agents.

Ultrasonic Desizing

To determine quantitatively the rate of desizing of various sizing agents, the test procedure used on a laboratory scale was to pour enough starch solution on to evaporation dishes so that 0.2 to 1.0 g of dried size remained after evaporation of the water. Less than 0.2 g did not provide sufficient accuracy; more than 0.7 g resulted in a thick deposit that caused portions of film to break and flake off in pieces. With enzyme-degraded starch, which had less adhesive characteristics, a fine mesh metal screen was placed on the evaporation dish to serve as a binding agent.

Visually, the ordinary starch resembled an insoluble plastic film that flaked off easily in one piece. The degraded starches formed an adhesive, soluble film that did not peel off the surface.

The evaporation dish was placed in a beaker, the ultrasonic transducer positioned approximately 1 cm above the dish, and the beaker was filled with water (Figure 8). The evaporation dish was weighed before and after the test.

The mass transfer rate (solubility, diffusion, and erosion) was lowest for degraded starch with a magnetic stirrer (washing machine action) in cold water (Table VII). The highest mass transfer rate was for degraded starches when used with ultrasonics at the ambient temperature (Table VII). The temperature of 40°C was a result of a small amount of heat generated by the transducer and water agitation. The ultrasonic power used in these laboratory tests was 75 W.

The laboratory-scale ultrasonic desizing was extended to industrial scale by using the generator and transducer system described in Figure 9 (Ultrasonic generator and transducer supplied by either Wave Energy Systems, Newton, Pa. or UE Systems, New York)*. Printcloths sized with fermented and enzyme-degraded starches were soaked in ambient temperature water for 15 minutes and given ultrasonic treatment for various lengths of time. The data for both degraded starches were equivalent and provided the curve of Figure 10. The laboratory scale transducers (Figure 8) provide a power density in the range of 12 kW/m^2 and would require a cloth velocity that would have a residence time of 0.5 seconds at the transducer to remove all the sizing agent. The large-scale transducers (Figure 9) provide a power density in the range of 6 kW/m^2 and require a cloth velocity that provides a residence time of approximately 1 second to remove the degraded starch.

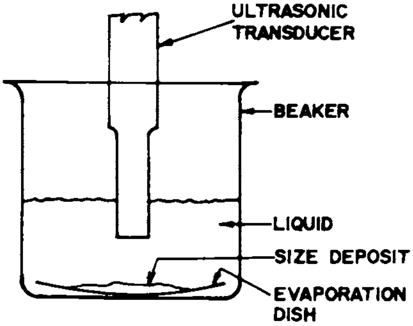


Figure 8. Mass transfer determination of evaporation dishes

Table VII. Rate of Size Removal

METHOD	CONDITIONS OF STARCH REMOVAL	MASS TRANSFER RATE G/HR.
1	STARCH, FERMENTED, 21°C	0.026
2	STARCH, 40°C, ULTRASONIC	1.3
3	STARCH, FERMENTED 80°C	3.8
4	STARCH, FERMENTED, 40°C, ULTRASONIC	6.7
5	STARCH, ENZYME, 40°C, ULTRASONIC	11.2

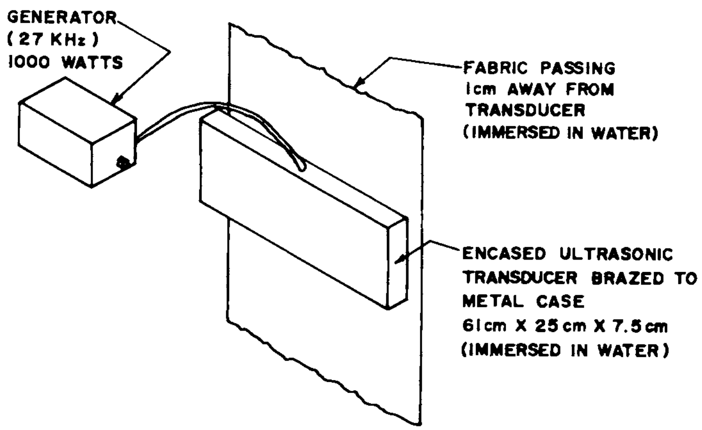


Figure 9. Ultrasonic desizing of fabric

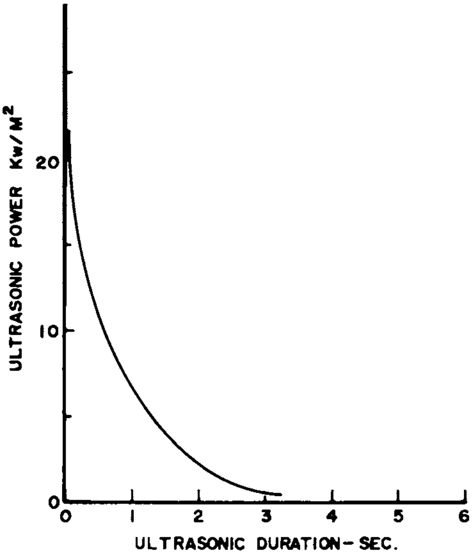


Figure 10. Desizing ultrasonic power vs. residence time (print cloth one cm distance)

BOD Tests of Starches

As part of an effluent study, the biochemical oxygen demand (BOD) of starches was evaluated. Starch solutions were stored in special BOD bottles, and the oxygen contents were analyzed during a period of 21 days. Order of decreasing oxygen demand was: ordinary starch, enzyme-degraded starch, and fermented starch. A study was also made to determine the effects of adding these starches to sewer water. The results were the same as above; the ordinary starch produced immediate reactivity, and the solution became putrid within five days. Both enzyme-degraded starch and fermented starch in sewer water showed resumption of degradation at a low reactivity level; however, the enzyme-degraded starch solution produced various forms of mildew and discolorations, indicating that the fermented-degarded starch represents a chemical structure already degraded by bacteria and thus is less prone to further degradation by bacteria. Further testing is planned.

Abstract

Textile sizing and desizing operations were investigated with energy conservation in mind. There was significant gain in energy conservation when fermented and enzyme-degraded starches were utilized. These degraded starches were tested on yarn both in the laboratory scale and in pilot plant industrial scale applications, and were found to be equivalent to conventional starch. Tests included the weaving of yarn treated with degraded starches. Degraded starches can be applied and washed from yarn at ambient temperatures; whereas, conventional sizing starch must be applied and washed from yarn at approximately 100°C. Evaluations of ultrasonic desizing procedures show that they require only a fraction of the energy needed for conventional desizing. Normal solubility was augmented with ultrasonics by induced ablation and diffusion. Favorable yarn qualities were achieved.

Literature Cited

1. Radley, J. A., "Starch Production Technology"; Applied Science Publishers: London (1976), pp 295-305, 456.
2. Hamby, D. D., "The American Cotton Handbook";Interscience Publishers: New York (1966), Chapter 15.
3. Whistler, R. L., and Paschall, E. F. "Starch: Chemistry and Technology"; Academic Press: New York (1967) Vol. I, pp 133-138, 251-278; Vol. II, pp 147-162.

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Energy and Related Savings from Controlled Low Wet Pick-Up Application of Textile Chemicals and Dyes via Semistable Foams

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Interest in low wet pick-up methods for textile finishing and dyeing has burgeoned since the oil embargo and resultant shortages in 1973-74. A partial listing of the methods employed includes: vacuum extractors (1), air jet-assisted squeeze rolls (2), kiss rolls (3), transfer belts (4), a blast of high velocity gas (the "machnozzle") (5), sprays (6), and foam coating (7, 8, 9). Primary impetus for most of these developments was the reduced energy required in subsequent processing steps, since evaporation of water is by far the most energy intensive step in textile wet finishing (10, 11) and dyeing (11).

Other substantial benefits derive from reducing the wet pick-up in wet finishing and continuous dyeing operations. Improved chemical efficiency in resin finishing has been reported by several sources (4, 12, 13, 14), while the relation of water content to dye migration tendency during the drying step of continuous dyeing has been recognized (15, 16). For a current review of prior art low add-on methods, see Leah (16a).

Methods which employ liquid phase treating liquors (spray, transfer rolls and belts, etc.) share a common difficulty stemming from the low volume of liquor in relation to the large surface area of the fibers comprising the substrate to be treated. This difficulty is acerbated when aqueous liquors are to be applied to hydrophilic fibers. Foam coating methods employ stable foams which allow the thickness of the liquid-air mixture to be controlled by a doctor blade or roll. Comparatively low add-ons can be achieved by virtue of the low density of the foam layer, but the stable nature of such foam, and its immobile liquid phase, inhibit rapid, uniform distribution through the substrate.

CONTROLLED LOW WET PICK-UP VIA SEMI-STABLE FOAMS

The use of semi-stable foams, which have a short half-life (i.e., time for half of the contained liquid to drain from the foam) of the order of a few minutes, has made possible a high speed process for uniformly impregnating fabrics with controlled,

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low wet pick-ups of foamed dyes, resins and other chemical substances (17, 18). The application of fast-wetting, semi-stable foams cannot be controlled by conventional coating methods, but requires the use of a novel applicator to control the foam-fabric contact time (19). The present paper describes results obtained by controlled, low wet pick-up applications of DMDHEU resin formulations and disperse dyes to fabric employing semi-stable foam finishing technology (the "FFT" Process).

Features of the FFT Application Process. The high speed FFT Process can be characterized by consideration of the key features of the feed liquor, foam and applicator system employed in the process.

Feed Liquor Characteristics:
- High concentration of functional chemicals (resin, dyes, softener, etc.)
- Rapid wetting of the substrate to be treated
- Formulated with foaming agents which product fast-breaking semi-stable foam

Semi-Stable Foam Characteristics:
- Half-life between about 1 and 60 minutes
- Density in the range 0.3-0.01 g/cc
- Bubble diameters in the range 0.05-0.5 mm

Applicator System Characteristics:
- Metered rate of delivery of liquor and air to the foamer, and of foam into the fabric substrate to be treated
- Applicator nozzle design to precisely control the foam-fabric contact time
- Nozzle design to deliver foam to fabric at a controlled rate and in a uniform state of relaxation across the width of the nozzle orifice

The foam-fabric contact time, or the machine contact time (MCT), is determined by the ratio of the nozzle orifice dimension in the direction of fabric travel to the fabric velocity:

$$\text{MCT} = \frac{\text{Nozzle Gap Length (cm)}}{\text{Fabric Speed (cm/sec)}}$$

For typical nozzle gap dimensions ($\sim$1 cm) and substrate speeds ($\sim 10^2$ cm/sec), MCT values are in the range 10^{-2} to 10^{-3} seconds.

Conditions for Uniform Substrate Coverage. Foam delivered in the FFT Process to a fabric substrate at a given add-on rate (per cent by weight) requires a certain time to break and absorb into the fabric. The rate of adsorption will depend on the foam composition and properties, and on the composition, structure and sorbancy of the fabric substrate under the conditions of application. For a given foam and fabric combination, the time required for a given add-on of foam to be absorbed is denoted as the Equilibrium Contact Time (ECT). As the rate of delivery of foam to the fabric is increased, ECT will, of course, increase. Figure 1 shows an operational method for defining ECT for a particular foam-fabric combination. The necessary condition for uniform coverage of the treated substrate is:

$$ECT \geq MCT$$

A steady positive pressure is maintained in the applicator nozzle when ECT > MCT.

For conditions where ECT < MCT, the foam is being applied under starved feed conditions, and coverage of the substrate is non-uniform, i.e., in spotty or wavy patterns.

RESIN FINISHING

Energy consumption in textile processing is summarized in Table I (20). As a result of conservation measures and more energy-efficient equipment in the U.S. textile industry, average energy consumption per pound of product decreased 12% between 1973 and 1978 (21).

TABLE I. Energy Consumption Per Pound of Product in Textile Processing (Adapted from 20)

Operation	Energy Consumed	
	BTU/lb	% of Total
Fiber to Finished Fabric	30-40,000	100
Wet Processing	15-30,000	40-70
Dyeing and Finishing	10-15,000	25-50

Table II shows the rapid rise in the cost of various energy sources between 1972 and 1977 (22, 23). Continuing escalation of prices can be expected; for example, the price of natural gas has been projected to rise by 1985 to a level 2.5 times its 1976 price (24).

The energy requirements for gas-fired oven drying of fabric have been estimated by Hebrank (10), whose results show that total energy requirements are nearly equally divided between that needed to heat and evaporate water from the fabric and that needed to heat the make-up air (24 lb. for each lb. of water evaporated) for the oven. BTU requirements per 100 lb. of dry fabric are tabulated in Table III for several moisture content levels of the fabric entering the oven, using the calculation method described by Wagner (11). Annualized energy requirements and costs are also

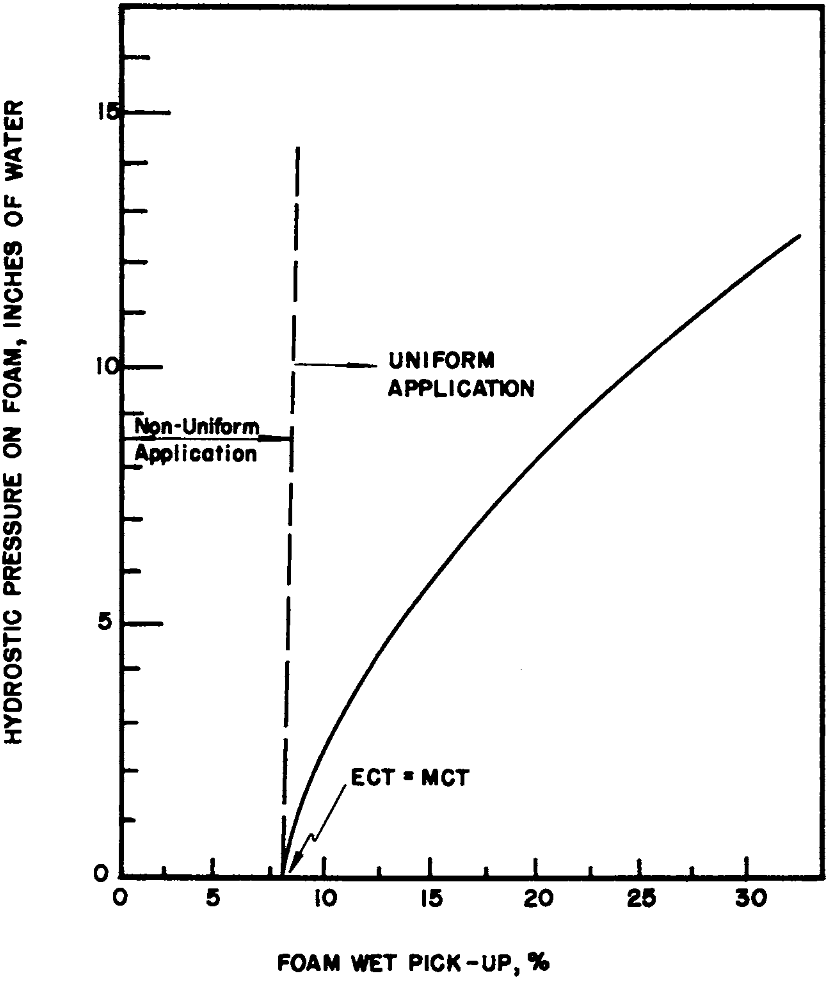

Figure 1. Operational definition of equilibrium contact time (ECT) in the FFT Process: fabric (65/36 polyester/cotton sheeting, 3.7 oz/yd^2); speed of fabric (100 ft/min); nozzle gap width (0.5 in.); machine contact time (MCT) (0.025 sec); foam (0.15 g/cc density, 46% solids content).

TABLE II. Changes in Energy Costs, 1972 to 1977
(Adapted from 22, 23)

Energy Source	Dollars Per Million BTU	
	1972	1977
Natural Gas	$0.80	$2.30
Fuel Oil (Aver. No. 2 and 6)	0.60	2.75
Coal	0.40	2.40
Electricity	5.25	7.50
Weighted Average	1.25	3.00

estimated in Table III, based on a yearly production rate of 19.4 million pounds of fabric (8 oz./linear yd. fabric, treated at 100 yd./min., 300 days/yr., 90% running efficiency) and natural gas cost of $\$2.50/10^6$ BTU. The calculated energy requirements can be reduced by employing heat exchangers to capture and recycle some of the heat contained in the exhaust air; however, since the calculations ignore inefficiency in energy conversion and heat losses, the values in Table III are probably representative for a modern finishing line.

Low Wet Pick-Up Foam Finishing. When applying textile resins as semi-stable foams by the FFT Process, the ingredients are ordinarily mixed in their commercial concentrations and foaming and wetting agents are applied without further dilution (25). For the application of 1,3-dimethylol-4,5-dihydroxy-2-imidazolidinone (DMDHEU) resin using typical Lewis acid catalysts (e.g., zinc nitrate or magnesium chloride), the solids content of the feed liquor is ca. 40-45%; thus, when applying 6% resin via the FFT Process, the co-applied water add-on is only about 9%. From Table III, the annualized savings in going from a pad bath application of resin at 60% moisture level to a foam application at 10% water add-on are estimated to be 21×10^9 BTU and $53,000.

Chemical and Related Savings. Improvement in resin efficiency when the finish is applied at low wet pick-up can be expected due to the reduction or elimination of migration during drying. If the reactants are applied uniformly, the absence of migration allows a lower average level of treatment to assure a given level of performance in the finished fabric. Experimental evidence for such an improved efficiency has been reported by several investigators (4, 13, 14). Results in our laboratories have confirmed a higher resin efficiency for polyester-cotton blend fabrics treated at low wet pick-up by controlled applica-

TABLE III. Tenter Frame Drying Energy Requirements as a Function of Moisture Content of Entering Fabric[a] (Adapted from 10, 11)

Step	Moisture Content =	Energy Requirement, M BTU/100 Lb. Fabric			
		80%	60%	40%	20%
Heat and Evaporate Water Raise temp. 70 to 212°F 100 x 1.0 (212-70)		11.4	8.5	5.7	2.9
Latent Ht. Evap. 970.3 x % Water		77.6	58.2	38.8	19.4
Raise Steam to 250°F 100 x 0.48 x (250-212)		1.5	1.1	0.7	0.3
Heat Air (24 lb. air/lb. water) 2400 x 0.243 (250-70)		83.9	63.0	42.0	21.0
TOTAL, M BTU/100 lb. fabric		174.4	130.8	87.2	43.6
M BTU Annualized[b]		33.8×10^6	25.4×10^6	16.9×10^6	8.46×10^6
$ M Annualized[b]		$84,500	$63,500	$42,300	$21,200

[a] Oven temperature - 250°F.

[b] Based on 19.4 million lb. fabric/yr. (see text) and $\$2.50/10^6$ BTU.

tion of semi-stable foams. These studies, which compared the rate of increase in crease recovery angle when fabrics were treated with increasing add-ons of DMDHEU resin by the conventional pad and FFT processes, indicated a resin efficiency advantage of 10 to 20 per cent for the low add-on semi-stable foam process. Additional chemical savings can be expected from the FFT Process due to the virtual elimination of pad bath drops and the consumption of only metered quantities of foamed treating liquor delivered into the fabric. Production experience in a major mill has confirmed the expected level of chemical savings. For the application of 6% owf of DMDHEU finish at a chemical cost of 1.2 cents/yd.^{2} to 19.4 million pounds of fabric (conditions assumed in Table III), annual savings from a 10 per cent improvement in chemical efficiency is ca. $90,000. Added cost from foaming and wetting agents is only about one-tenth this amount.

Additional benefits to be realized from the low wet pick-up foam application method include greater line speed (especially where the dryer represents a bottleneck in the pad process to be replaced), lower pollution abatement costs due to reduced volumes of effluent and exhaust gases and reduced water consumption. The latter benefit becomes particularly significant where one or more conventional process steps can be combined or eliminated (e.g., co-application of resin and colorants, wet-on-wet applications, elimination of afterwashing, etc.).

CONTINUOUS DYEING

Steps in conventional continuous pad-thermosol dyeing, e.g., for polyester fabrics, are: (a) pad application of dyes and auxiliaries; (b) infrared predrying to about 30% moisture; (c) hot can drying; (d) thermofixing at 375-425°F; (e) afterwashing, where topical finishes may be applied in the final rinse; and (f) hot can drying. For blends, an additional chemical pad step following thermofixation may be needed to apply fixing or coupling agents for the cellulose dyes, followed by a steaming step to complete the fixation. In some cases, two passes down the range may be employed.

The most energy intensive steps in the process are the infrared predrying step, where the water content of the fabric is reduced to an intermediate level, and the subsequent drying steps. The data of Wygand (24) indicates that a typical infrared predryer requires about 4,250 BTU per pound of water evaporated, compared with a comparable figure of about 2200 BTU per pound of water for an efficient gas fired oven (10, 11). The infrared heating step, which may employ either gas or electrical energy, is needed to achieve a uniform, rapid drying rate without causing migration; the level of moisture to which the fabric is dried is typically about 30-35% for polyester-cotton blends (24).

Low Wet Pick-Up Foam Dyeing. Using concentrated dye liquors formulated with appropriate dispersing, foaming and wetting agents, dyes can be applied by the FFT Process at low wet pick-up levels which greatly reduce or eliminate the need for predrying. Most experience to date has been confined to disperse, reactive and acid dyes applied on a narrow (10 inch) width pilot line, although fabrics up to 50 inches wide have been dyed on a development scale with good results. Wet pick-ups have ranged from about 10 to 35%, depending on the depth of shade and dye class. Deeper colors generally require higher wet pick-up due to present limits on the dye concentrations which can be formulated and the more severe uniformity requirements in the deeper shades.

The low wet pick-ups demonstrated for dye application with semi-stable foam should eliminate the need for the infrared predryer, since migration is virtually eliminated (17). Using Wygand's data (24) for energy consumption in the predryer and a production rate of 2500 lb. of fabric per hour, this would represent an energy savings of 3.4 x 10^6 BTU/hr. or about 21 x 10^9 BTU annually for the case when the wet pick-up of the reference pad process is 60%. The resultant dollar savings will range from about $50,000 for a gas fired infrared unit to as high as $150,000 for an electrically powered predryer, based on 2.5 cents/KWh (see Table II for energy costs).

By using disperse dye liquid concentrates which have thermofixation of 95% or greater (26), polyester fabrics can be foam-dyed at very low wet pick-ups (e.g., 15-20% for medium-deep shades) without need for afterwashing. The resultant annualized per-line energy and cost savings are estimated, using Wygand's data (24), to be 30 x 10^9 BTU and $75,000, respectively.

Successful laboratory and development scale union dyeings of cotton-polyester blends have been made by the FFT Process, employing recently introduced reactive and disperse "T-dyes", which can be applied from the same liquor and fixed under similar conditions (27). Very attractive energy savings can be realized from the foam application of this dye system, in comparison with the conventional two-pad procedure for continuous dyeing of blends. Higher dye costs involved in using either the T-dyes or the disperse dye concentrates would counterbalance only a minor portion of the total savings.

Chemical and Other Related Savings. Laboratory studies of dye migration as a function of wet pick-up on fabrics dyed from semi-stable foams show that for wet pick-ups below about 30%, migration is virtually eliminated and that an antimigrant thickener is no longer needed. Elimination of this auxiliary, normally employed at about 0.2% based on the fabric weight and costing about $2 per dry lb., would represent annualized savings of about $65,000 for a typical continuous thermosol range operating at an hourly rate of 2500 lbs. (300 days/yr. at 90% efficiency).

As in the case of resin finishing, the reduced wet pick-up from foam application should allow increased line speed in continuous dyeing. The extent to which such a production rate improvement can be realized in practice will depend on the rate-limiting step in the continuous process. Whenever drying rates limit the capacity of conventional pad application processes, replacement of the pad with a semi-stable foam applicator will allow dramatic speed increases. Should the final drying step following afterwashing remain as a bottleneck in a converted continuous dye range, the use of vacuum extractors (1), special squeeze rolls (2, 23) or other expression methods (23) to lower the moisture content of the fabric entering the dryer will pro-vide further savings.

Literature Cited

1. Anon., product literature from suppliers: IMMS Machinery Co., Greenville, So. Carolina; Gaston County Dyeing Machine Co., Mount Holly, No. Carolina.
2. Lauzier, M. V., "An Update on Hydro-Extraction Via the Roller Jet Squeezer", presented at the 1975 National Technical Conference, Amer. Assoc. of Textile Chemists and Colorists, Chicago, Illinois, Oct. 16, 1975.
3. Bruno, J. S. and Blanchard, E. J., "Economical Kiss Roll Padding", Amer. Dyest. Rept. (1977), 46-50.
4. Burkitt, F. H., "Can Cotton Take the Throne Again?", Text. World, (1974), 124, 167-177.
5. Theusink, M., "The Machnozzle: An Application of Sonic and Supersonic Vapor Flows in Textile Finishing", presented at 1976 National Meeting of Amer. Assoc. of Textile Chemists and Colorists, Montreal, Canada, October 12-15, 1976.
6. Hoechst A. G., "Process and Device for the Continuous Fixation of Prints and Pad-Dyeings on Polyester Fibers and Their Mixtures With Cellulose Fibers", U.S. Patent 3,973,902 (Aug. 10, 1976).
7. Interchemical Corp., "Process of Coloring Textile Materials", U.S. Patent 2,971,458 (Feb. 14, 1961).
8. United Merchants and Manufacturers, "Method for Treating Fabrics", U.S. Patent 4,118,526 (Oct. 3, 1978).
9. Hoechst A. G., "Device for the Application of Foam on Textile Webs", U.S. Patent 4,061,001 (Dec. 7, 1977).
10. Hebrank, E. H., "Options for Reducing Fuel Usage in Textile Finishing Tenter Dryers", Amer. Dyest. Rep. (1975) 32-37.
11. Wagner, R. E., "Energy Conservation in Dyeing and Finishing", Text. Chem. Color. (1977) 9, 52-54.
12. Miro, P., et al., "The Distribution of Crosslinks in Easy Case Fabrics", Text. Chem. Color. (1972) 4, 271-274.

13. Turner, J. D., et al., Northern Piedmont Section, "Improved Properties of Cotton Fabrics Prepared From Ring Spun and Open-End Spun Yarns", Text. Chem. Color. (1977) 9, 250-258.
14. Triatex International A.G., "Method and Apparatus for Finishing Cellulose-Containing Textile Materials and Textile Materials Thus Produced", U.S. Patent 3,811,834 (May 21, 1974).
15. Etters, J. N., "Continuous Dyeing of Polyester Knits", Modern Knitting Management (1973) 24-30.
16. Etters, J. N. and Urbanik, A., "Particulate Activation of Disperse Dye in the Thermosol Process", Text. Chem. Color. (1977) 9, 102-108.
16a. Leah, R. D., "Controlled Low Add-On Application of Finishing Liquors in Easy-Care Finishing", Text. Inst. and Indust. (1978), 395-399.
17. Bryant, G. M., Rankin, W. W. and Walter, A. T., "Foam Finishing Technology (FFT): A Low Energy Process for Textile Finishing and Dyeing", presented at 43rd Annual Textile Research Institute Research and Technology Conference, Atlanta, Georgia, April 6, 1978.
18. Clifford, F., "Foam Finishing Technology: The Controlled Application of Chemicals to a Moving Substrate", Text. Chem. Color. (1978) 10, 37-40.
19. Union Carbide Corp., "Apparatus for Application of Foam to a Substrate", U.S. Patent 4,023,526 (May 17, 1977).
20. Jones, D. M., "Energy in Textile Processing", Seventh Shirley Institute International Seminar, Manchester, England, (1974) Publication S-11, 35 pp.
21. Pederson, A. T., "Need for Energy Conservation Challenge for Mills, Machinery Mfrs. and Designers", Daily News Record, Jan. 30, 1978, 38-39.
22. The Conference Board, "Road Maps of Industry", (Dec. 1977) No. 1821, Washington, D.C.
23. Goldstein, H. B., "Low Wet Pick-Up Finishing", paper presented at 1978 National Meeting of Amer. Assoc. of Textile Chemists and Colorists, Anaheim, California, Nov. 1-4, 1978; Book of Papers, pp. 275-282.
24. Wygand, W., Jr., "Conserving Energy in Continuous Dyeing", Text. Chem. Color. (1978) 10, 30-33.
25. Union Carbide Corp., "Foams for Treating Fabrics", U.S. Patent 4,099,913 (July 11, 1978).
26. Schlaeppi, F., "Novel Approaches to Energy Conserving Dyeing and Printing Processes", 176th Amer. Chem. Soc. National Meeting, Cellulose, Paper and Textile Division; Miami Beach, Florida, Sept. 11, 1978.
27. Graham, L. A. and Suratt, C. A., "T-Dye System: Basic Advance in Continuous Dyeing of Blends", Amer. Dyest. Rep., (1978) 36-47.

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The Utilization of Foams in the Wet Processing of Textiles

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The textile industry presently consumes 0.32 QBtu per year, the energy equivalent of 55 million barrels of oil (1). It has been estimated that 55 to 60% of this energy is used in the desizing, bleaching, dyeing and finishing of fabrics. During the course of these operations, a fabric is subjected to several wetting and drying operations. Thus, in the face of the energy crisis, it is not surprising that during the last several years, considerable effort has been spent on developing methods for reducing the amount of energy consumed in the wet processing of textiles.

One approach has been to increase the energy efficiency of conventional processing by such techniques as improved energy conversion processes, energy reclamation and recycle and mechanical techniques to extract a greater portion of the water from wet fabrics prior to their being dried.

The second approach has been to devise waterless or reduced-water techniques for the application of finishes or coloring agents to fabrics.

Waterless techniques include solvent dyeing and finishing, powder dyeing and "100% solids" systems. Solvent dyeing and finishing received a great deal of attention during the sixties but unfavorable distribution coefficients of most dyes between solvent and fabrics and the need for highly efficient solvent recovery systems has limited commercial development (2).

The application of color to a substrate in the form of a spray of finely divided colorant is an accepted practice for metal coatings (3,4). The feasibility of dyeing polyester fabrics by the application of powdered disperse dyes to the fabric has been demonstrated (5); however, many development problems such as efficient recovery of unfixed dye and the homogeneous application of dye mixtures need to be resolved. Likewise, the use of "100% solids" systems as, for example, radiation-cureable finishes will also require considerable development work.

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At United Merchants Research Center, we have chosen to concentrate our efforts on developing wet processing methods which use significantly less water than conventional wet processing methods. The function of water in finishing is to uniformly distribute a relatively small amount of chemicals throughout the fabric. Instead of water, air is used as the main diluent and a concentrated mixture of the finishing agents or colorants is applied as a spray or foam.

The objective of this paper is to describe the United Merchants and Manufacturers continuous foam processing method for the finishing and coloring of textiles. The term "continuous" is used to distinguish it from the batch foam dyeing process known as the Sancowad^R process developed and commercialized by the Sandoz Colors and Chemicals Co. (6).

Foam processing is versatile; it can be used for the dyeing, printing and finishing of fabrics. The process is not limited by fiber type or construction. Fabrics ranging from polyester ninons to 48 oz./square yd. nylon carpet have been successfully dyed on a pilot range. Foam finishing of light weight flat goods, flannels, corduroys and upholstery fabrics is being commercially practiced (7). Flat goods, flocked fabrics, tubular knits, terry cloth have been printed on both rotary screen and roller printing production ranges. Conventional continuous finishing or dyeing ranges can be converted to foam ranges by incorporation of a mechanical foamer and a device for application of the foam to the fabric. Capital expenditure is very modest. The mechanical foamers are of the type that are used to create foamed backcoatings for carpets and drapery. Thus much of the technology associated with the foaming of aqueous systems is already familiar to many finishing plants.

The energy savings potential of foam processing is self-evident; the less water that is applied to the fabric, the less that must be later removed by evaporation (8).

A wide variety of compositions, as illustrated in Table I, have been foamed and applied to fabrics.

Table I. Foamable Compositions

1. Aqueous Solutions and Dispersions
    a. resins
    b. hand builders
    c. dyes
    d. softeners
2. Solvent/Water Emulsions
    a. pigment printing
3. "100% Solids"
    a. reactive fluids
    b. plasticizers

The systems are listed in the decreasing ease of formulating foamable systems which will yield foams of the proper stability for foam processing of textiles. While completely non-aqueous foamable systems have been used to apply finishes under laboratory conditions, none have yet been developed that can be handled in a finishing plant environment. Since "100% solids" systems represent the ultimate in energy savings, efforts in this area are continuing.

The present discussion will be limited to aqueous systems.

Discussion

Foam Formulation

The factors to be considered in the formulation of foamable compositions are outlined in Table II.

Table II. Factors Involved in Foam Formulating

1. Interaction of foaming agent with finish components.
2. Influence of foaming agent on finished fabric.
   a. esthetic
   b. physical properties
3. Desired stability of composition.
   a. unfoamed concentrate
   b. foamed composition
4. Cell structure of the foam.

The foamable compositions are designed so that the foam can be easily collapsed after being applied to the fabric. The degree of stability and ease of collapse of the foam are dictated by function and application mode of the finish (Table III).

Table III. Factors Involved in Stability of Foam Composition

1. End Use
   a. printing
   b. dyeing
   c. finishing
   d. special effects
2. Fabric
   a. fiber composition
   b. construction
3. Other
   a. wet add-on
   b. degree of penetration into fabric

If the foamable composition is to be used for printing, the composition is designed to have a useful life of 8 to 10 hours after foaming for a very practical reason. For a multicolor printing operation, it would be impractical to have a mechanical foamer for each color being applied to the fabric. Instead each foamed color composition is sequentially prepared in the color shop. The foamed colors are then treated as conventional print pastes and applied to fabric by either screen or intaglio printing techniques.

Thus foamable systems for printing normally contain, in addition to the foaming agent, an additive to stabilize the foam.

A foamable formulation for continuous dyeing requires less stability in the foamed state. The foam is generated continuously at a rate equal to its consumption on the dye range. The foam must be sufficiently stable to survive during the application step.

Depending on the mode of application, foamed dye formulations should have half-lives of 30 to 180 minutes as determined by the method of Bikerman (9).

For example, if a knife coater is used, the foam must be sufficiently stable to form a stable rolling bank behind the coating knife. Should the foam begin to collapse prematurely, uneven dyeing will be the result.

Foam stability is less critical for resin finishing or hand modification. However, it must not collapse prior to application on the fabric otherwise the composition will act like a conventional finish and result in high wet pick-ups.

For foamed finishes, the half life can be as short as 5 minutes.

In all cases, it is obvious that the foaming agent must not adversely effect fabric esthetic or physical properties. The latter has been relatively simple. In general we have not seen any deterioration of fabric physicals in foam finishing. In fact, in the durable press finishing of sheeting fabrics, dusting is significantly less with the foamable finish. We believe that this is a result of less finish residing on the face of the fabric. With less water present there is less tendency for resin migration during drying.

Esthetic properties can be altered by foaming agents. For example, the resiliance of finished fabrics is altered by the presence of the foaming agent. A durable press finish formulated with a Kritchevsky base foaming agent imparted a limp hand to a polyester/cotton lightweight woven fabric, while the same finish formulated with a sulphated arylpolyethoxyethanol gave a resilient hand. As yet we have no hard and fast rules for matching foaming agent to desired esthetics, although one obvious rule of thumb is that it is preferable to use very small amounts of highly active foaming agents.

Care must be taken that finish systems not contain defoamers or foam destabilizers. Polyvalent metal salts are often used as catalysts in resin systems and several of these, such as zinc nitrate, strongly inhibit foam generation. This is not dissimilar to the foam inhibiting action of hard water on fatty acid soaps.

Foam Application

For continuous foam dyeing or foam finishing, an unfoamed concentrate consisting of the dyes, dyeing auxiliaries and/or the finishing chemicals and the foaming system is fed to a mechanical foamer where air is injected into the agitated liquid. The foam is then transferred to the coating station through a flexible hose. Several of the methods by which the foam can be applied to the fabric are listed in Table IV. The choice is dictated by the fabric construction and effect desired.

Table IV. Foam Application Techniques

Knife Over-Roll Coater
Horizontal Pad Coating
Floating Knife Coater
Extrusion Coating

For the dyeing or finishing of pile fabrics, such as carpets, flocked goods, velvets or sliver knits, the foam can be applied to the face of the fabric by means of a knife over-roll or knife over table coater (Figure 1).

For the finishing of flat goods, where uniform application to both sides of the fabric is required, a horizontal pad can be used (Figure 2). In this case, a reservior of foam is maintained on both sides of the fabric, the two rolls and two end dams acting as a box to contain the foam.

In cases where either of these techniques would adversely affect the esthetics of the face of the fabric, the foamed finish can be applied to the back of the fabric by means of a floating knife.

The foam prior to collapse normally sits on the surface of the fabric; however, once the foam collapses there is a precipitous drop in viscosity and the resultant liquid rapidly flows along the fibers uniformly sheathing them with the dye or finish liquor. This is illustrated in Figures 3 and 4.

Figure 3 is a photograph of the cross section of a pile fabric to which a foamed dye composition has been applied. The foam sits on the face of the pile. In Figure 4 is a similar cross section but after the foam has been collapsed.

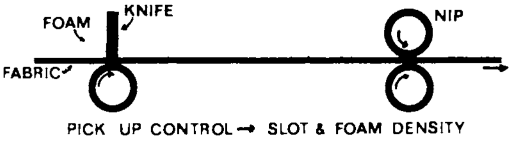

Figure 1. Knife over roll coater.

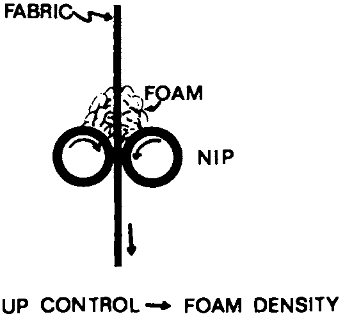

Figure 2. Horizontal pad applicator

In Energy Conservation in Textile and Polymer Processing; Vigo, T., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 1979.

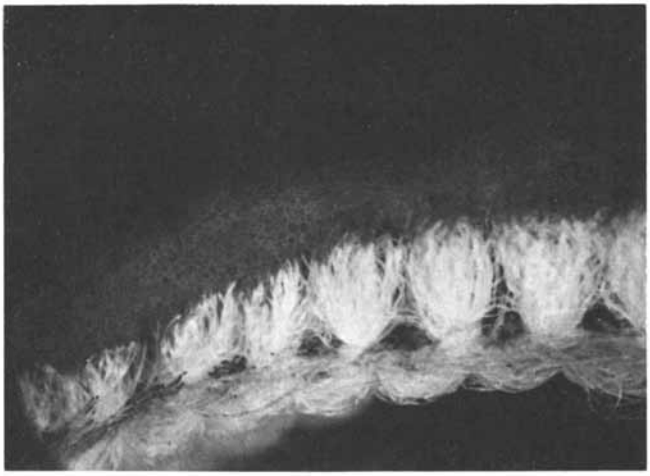

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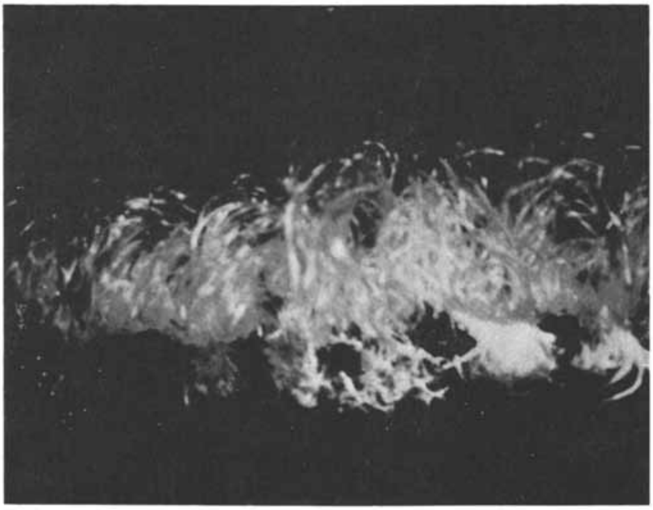
Figure 3. Foam coated carpet before foam collapse (13)



American Dyestuff Reporter

Figure 4. Foam coated carpet after foam collapse (13)

Each fiber bundle has been sheathed with dye liquor but there is no excess liquor between the bundles. Thus after drying and fixing, there is no excess color remaining to cause crocking problems or which must be removed by an afterwash.

In the foam process, a concentrated solution of the finishing chemicals compounded with suitable foaming agents and, if necessary, foam stabilizers is mechanically foamed so as to incorporate by volume 50 to 95% air. This foam, having an appearance quite similar to shaving cream, is applied to the fabric. The foam-coated fabric is then subjected to a mechanical pressure which collapses the foam. The fabric is then dried and cured in the conventional manner.

The degree to which the water of a finishing or dyeing formulation can be replaced by air is limited only by the amount of water required to produce a reasonably stable dispersion of the finishing chemicals and for cellulosic fabrics that amount of water required to swell the fibers. As much as 65% of the water has been removed from typical durable press finishes.

The amount of dry add-on of finish or color is controlled by:

a. the concentration of active ingredients in the unfoamed composition.
b. the blow ratio.
c. the volumetric add-on of foam onto the fabric.

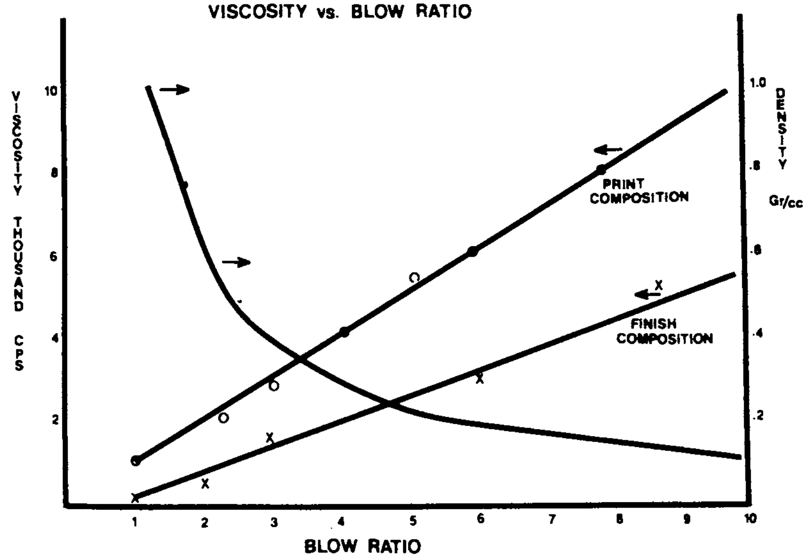
The unfoamed mixture should be as concentrated as possible, consistent with mix stability, in order to minimize wet add-on and to maximize energy savings.

The blow ratio is the ratio of the weight of the unfoamed composition to the weight of an equal volume of the foamed composition. The relationship between air content of a foam, the blow ratio and the foam density is illustrated for an unfoamed composition having a density of 1 g/cc in Table V.

Table V. The Relationship of Blow Ratio to Foam Density

Liquid(%)	Air(%)	Density (g/cc)	Blow Ratio
100	0	1.0	1
20	80	0.2	5
10	90	0.1	10
6.6	93.4	0.066	15

A high blow ratio is desired since this creates a large volume of foam with respect to the solids. This serves to minimize variation in dry solids add-on due to variances in knife setting or non-uniform pressure between the two horizontal pad rolls. However, the apparent viscosity of the foamed composition is directly proportional to its blow ratio (Figure 5) and the fabric weight and construction will dictate the best coating viscosity for that particular fabric.



Textile Chemist and Colorist

Figure 5. Viscosity and density of a foam as a function of the blow ratio (12)

The volumetric add-on of foam can also be used to control the dry pick-up on the fabric when the application method is knife coating. But for horizontal pad application, dry pick-up is best controlled by the blow ratio.

Results

Foam Finishing

In the textile industry, the term finishing is used to denote the application of chemicals exclusive of coloring agents to impart certain esthetic effects such as drape, handle or wrinkle resistance and to affect physical properties such as resistance to shrinkage, resistance to seam slippage or soil and stain resistance.

In conventional continuous wet finishing, a rather dilute, usually from 4 to 8% solids solution or dispersion of the chemicals is prepared. The fabric is then immersed in this solution. The wet fabric is passed through pad rollers to squeeze out the excess solution. Despite the squeezing, a cotton fabric usually retains 80 to 100% on the weight of the fabric of the finishing solution. For polyester-cotton blend fabrics, the wet pick-up is normally 50 to 80% on the weight of the fabric.

In continuous foam finishing, a concentrated solution containing the finishing chemicals and a suitable foaming system is mechanically foamed and the precise quantity of foam is applied to the fabric.

In Table VI, a conventional durable press finish bath composition is compared to its foamable counterpart.

Table VI. Typical Finish Baths (Solids Basis)

Components	Conventional	Foam
Resin	3-5%	6-15%
Emulsion Polymer	0-5%	0-15%
Softener	1-3%	3-10%
Catalyst	0.5%-1.0%	1-3%
Foaming Agent	- - -	0.1%-1.0%
Wet Pick-Up	50-100%	15-35%

For the plant trials which will be subsequently discussed, a 7% solids durable press, fabric stabilization conventional finish and a 14% solids foamable counterpart were applied to polyester/cotton fabrics of various weights.

The foam trials were conducted by breaking into conventional finishing production runs (which served as controls) and applying the finish as a foam. The only dryer conditions varied were temperature and through-put. No attempts were made to optimize air flow or the degree of air recirculation in the dryer. The foam was applied by means of a horizontal pad.

The operating conditions for the conventional production runs were established commercial practices and represent the best practical combination of oven temperature and range speed for effective drying of fabric for that particular range.

Since about 54% less water was used in applying the foamed finish to the fabric, energy savings of about 54% were anticipated.

Table VII summarizes the plant data where this finish was applied to a 3 oz./sq. yd. printed polyester/cotton fabric. In the first and second trials (columns 1 and 2), the dryer temperature was maintained at 350°F. in order to overcome a heat set put into the fabric during a high temperature curing of the printed pigments. In the third trial (column 3) where the dryer was used only for drying the fabric, it was possible to operate the dryer at its lowest temperature and still increase range speed.

Table VII. 50/50 Polyester/Cotton (wt. 3 oz./yd.^{2})

	Conventional	Foam	Foam
Finish Pick-Up on Wt. of Fabric	60%	30%	30%
Calculated Water Pick-Up	56%	26%	26%
Oven Temperature°F.	350	350	225 [a]
Speed, yds./min.	92	98	115 [b]
Speed Change		+6.5	+25
Nat. Gas Consumption (ft.^{3}/yd.)	1.38	0.71	0.39
BTU/yd.	1428	734	403
Energy Savings		47.6%	

[a] Minimum operating temperature

[b] Maximum speed

The same finish (Table VI) was applied to a heavier (6.6 oz./yd.^{2}) polyester/cotton fabric. Again, it was possible to reduce oven temperature and increase range speed and demonstrate significant energy savings. The data are summarized in Table VIII.

Table IX summarizes the results of a number of trials in which a durable press, fabric stabilization finish was applied to polyester cotton fabrics of various weights. The major conclusion to be drawn from this work is that while productivity (range speed) was significantly improved by switching to foam finishing, energy savings were less than predicted on the basis of a 54% reduction in amount of water applied to the fabric.

Table VIII. 50/50 Polyester/Cotton (wt. 6.6 oz./yd.^{2})

	Conventional	Foam
Finish Pick-Up on Wt. of Fabric	60%	30%
Calculated Water Pick-Up	56%	26%
Oven Temperatures°F.	350	250
Speed, yds./min.	57	110
% Speed Change	- -	+93%
Nat. Gas Consumption (ft. ^{3}/yd.)	2.26	0.31
BTU/yd.	2339	326
Energy Savings	- -	86%

Table IX. Dryer Data for 50/50 Polyester/Cotton

Fabric Wt. (oz./yd.^{2}) =	2.5		4.0		7.5	
	Conventional	Foam	Conventional	Foam	Conventional	Foam
Finish Pick-Up (On Wt. of Fabric)	60%	30%	60%	30%	60%	30%
Calculated Water Pick-Up	56%	26%	56%	26%	56%	26%
Oven Temperatures°F.[a]	320/340/ 340	320/340/ 340	320/350/ 360	320/350/ 360	330/370/ 380	330/370/ 380
Speed, yds./min.	51	89.5	46	94.6	40	80.7
% Speed Change		+75		+105%		+101%
Liquid Propane Consumption (ft.^{3}/yd.)	.0017	.0012	.0018	.0011	.0021	.0013
BTU/yd.	1163	821	1231	752	1437	889
Energy Savings		29%		39%		38%

[a] Three Zone Dryer

As the data in Tables IX, X and XI demonstrate, maximum energy savings are achieved only by a combination of reduced oven temperatures and higher range speeds.

Table X. Application of a Softener to 100% Flannel (Fabric wt. 2.7 oz./yd^2)

	Conventional	Foam
Finish Pick-Up On Wt. Of Fabric	68.4%	25%
Calculated Water Pick-Up	67.6%	24.4%
Oven Temperatures °F.	345/380	260/265
Speed, yds./min.	60	107
% Speed Change		78.3%
Nat. Gas Consumption (ft.^{3}/yd.)	0.409	0.089
BTU/yd.	423	92
Energy Savings		78.2%

Table XI. Application of a Durable Press Finish to Polyester Cotton Print Cloth (Fabric wt. 3.2 oz. yd.^{2})

	Conventional	Foam
Wet Pick-Up On Wt. Of Fabric	60	30
Oven Temperature °F.	350	225[a]
Speed, yds./min.	92	115[b]
% Speed Change		+24%
Energy Savings		73.6%

[a] Lowest operating temperature for this range.

[b] Maximum speed for this range.

It is evident from the data, that under present plant operating conditions, the dryer temperature has a greater impact on energy savings than has the increased range speed. The factors leading to less energy savings at high dryer temperatures include greater wall losses due to the temperature differential between dryer and plant temperature. But the most important factor is the energy consumed in heating large volumes of air to the higher temperature.

If energy savings is to be the prime consideration, this will be best achieved by drying the cloth at low temperatures and high speeds and then curing the cloth in a separate oven where there is little or no air flow through the curing chamber.

However, the ultimate objective should be the development of low temperature curing systems which do not require a separate high temperature (250-350°F.) curing step. One approach is radiation-cureable systems.

Foam Dyeing

The commercialization of foam dyeing has not progressed as far as foam finishing. As would be expected, uniform application of color is very critical and the critical step in foam dyeing is not the foam formulations but the mode of application of the foam to the fabric.

As shown in Table XII, a broad spectrum of fibers have been successfully dyed in the laboratory with a wide variety of dye classes. A significant process advantage as well as energy savings aspect is the observation that in most cases, the fabrics do not need a back-wash to remove unfixed dyestuffs. The unwashed dyed goods meet all commercial standards for crock and wash fastness. The only exceptions to the no back-wash requirement are in the cases of reactive, sulfur, azoic and pre-metallized dyes.

Table XII. Foam Dyeing

Fiber	Dye Classes
Polyester	Pigments, Disperse
Nylon	Acid, Disperse, Premetallized
Cotton/Rayon	Direct, Reactive, Sulfur, Azoics, Pigments, Vats
Acrylic	Cationic
Modacrylic	Cationic, Disperse
Acetate	Disperse, Pigments
Cotton/Polyester Blends	Direct/Disperse, Pigments

The greatest progress in foam dyeing has been in the area of carpets. Continuous foam dyeing of three foot wide carpet has been carried out on the pilot range. The foamed dye liquor was knife coated onto the carpets at wet pick-ups ranging from 30 to 70%. After the foam was collapsed, the color was fixed by steaming and the carpet dried. Except in the case of deep shades, no backwashing was required.

The rheology of foams coupled with the proper applicators permits the creation of unique random coloring effects not easily achieved by conventional dyeing methods. Carpets are particularily well suited for the production of random coloring effects.

As shown in Table XIII, the blow ratio of the foamed dye liquor is dictated by the face fiber weight of the carpet.

Table XIII. Carpet Dyeing

Carpet Wt. (oz./yd.^{2})	Blow Ratio
10-15	8:1 - 10:1
15-30	7:1 - 8:1
30-52	4:1 - 5:1

Although, actual energy consumption data has not yet been obtained, it is estimated that continuous foam dyeing of carpet will consume only 50% as much energy as conventional continuous dyeing (10).

Foam Printing

Foam printing of textiles has been disclosed in the patent literature (11).

Foam printing compositions have been devised which can be applied on conventional roller print or rotary screen print machines (12). These systems are not yet commercial.

In addition to energy savings, foam printing has several other advantages over conventional printing (Table XIV).

Table XIV. Advantages of Foam Printing

Faster Printing Speeds
Softer Hand
Less Strike Through
Uniform Coverage
Elimination Of Afterwashing

One striking feature of printing with foams has been the exceptionally soft hand. In conventional printing, a continuous film of color is applied to the fabric which tends to glue the fibers together resulting in a stiff or raspy hand. On the other hand, in foam printing no gums are used but rather the blow ratio controls the print paste viscosity. Once the printed foam has collapsed, its viscosity drops markedly permitting the color to flow down the fibers.

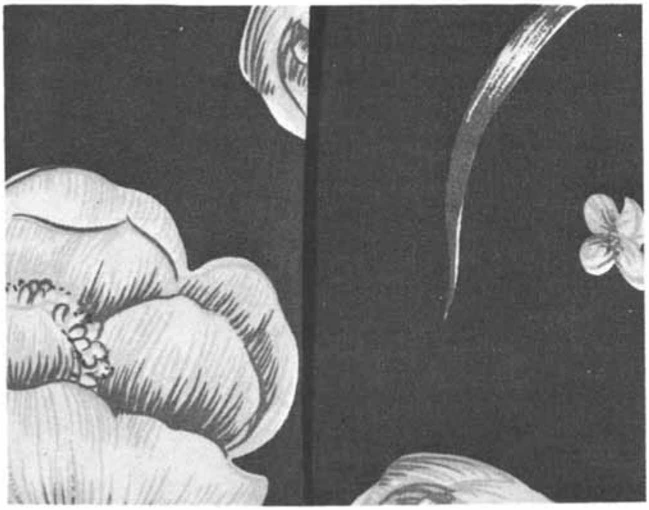


Figure 6. Rotary screen printing: (left) foam; (right) conventional

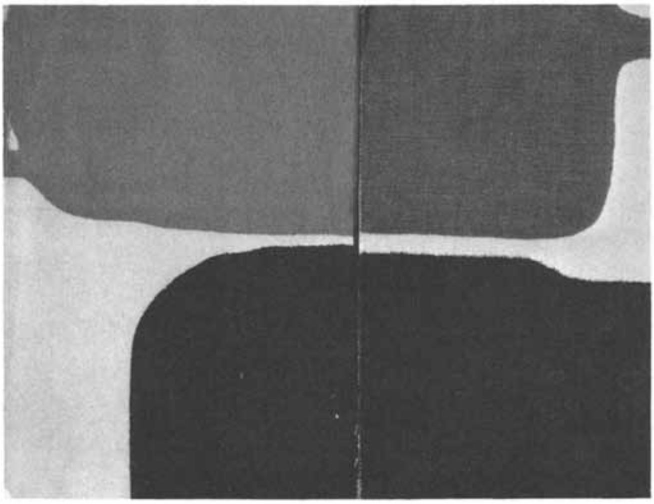


Figure 7. Rotary screen printing: (left) foam; (right) conventional

Figure 8. Engraved roll printing: (left) foam; (right) conventional

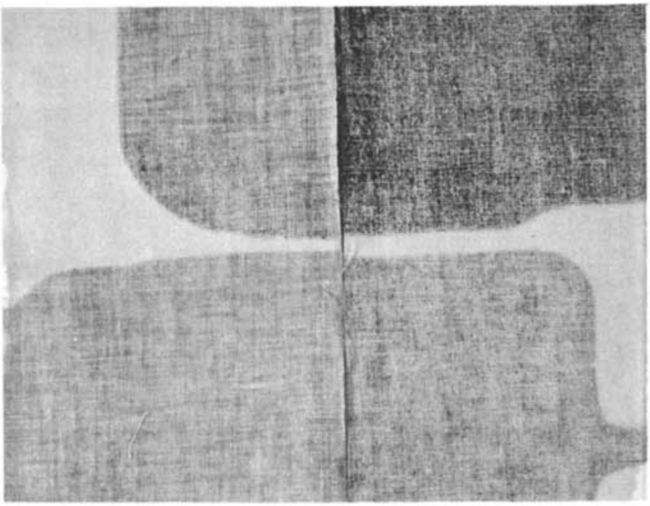


Figure 9. Backside of printed fabric of Figure 8: (left) foam; (right) conventional

Because of the low wet pick-up, there is no loss in print definition upon collapse of the foam. Because no thickeners are used in the print paste, after washing is not necessary in most cases.

The low wet pick-up of foam processing permits "wet-on-wet" applications. For example, foam printed fabrics have been foam finished without an intermediate drying. There was no loss in print definition as would be the case if conventionally printed goods were conventionally finished without first drying and curing the print. Thus an entire drying/curing step is eliminated.

Wet dyed goods have been foam finished. Conventional wet finishing of such goods would lead to color bleeding into the finish bath as well as dilution of the finish bath due to transfer of water from the fabric to the bath.

Figures 6 through 8 show the print quality of foam printing versus conventional. Figure 9 illustrates the reduction of strike through on foamed printed goods. The fabrics illustrated were printed on production equipment.

Acknowledgements

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Literature Cited

1. Suchecki, S., Text. Ind. (1975) 140 (10), 25.
2. Textile World (1973) 123 (2), 85.
3. Nylen, P. and Sunderland, E.,"Modern Surface Coatings",631; Interscience Publishers: New York, 1965.
4. Landrock, A., "Encylopedia of Polymer Science and Technology" 3,786; Interscience Publishers: New York, 1965.
5. Gregorian, R., and Namboodri, C., unpublished work.
6. Am. Dyest. Rep.(June 1973), 52.
7. Carter, T., Am. Dyest. Rep.(December 1978), 48.
8. Suchecki, S., Text. Ind. (1975) 140 (10), 57.
9. Bikerman, J., "Foams",161; Springer-Verlag: New York, 1973.
10. Namboodri, C. and Gregorian, R., Am. Dyest. Rep. (June 1978), 24.
11. Kumins C., Fine, J., and Chase V., U.S. Patent 2 971 458, (1961).
12. Namboodri, C., Johnson, J., and Gregorian, R., Text. Chem. and Color. (1978) 10 (10), 213.
13. Namboodri, C. and Gregorian, R., Am. Dyest. Rep. (June 1978), 31.

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Low Energy Curing Pigment Padding and Printing: Use of A Highly Active Catalyst System

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Pigment padding and pigment printing techniques are becoming increasingly popular throughout the world (1,2,3,4). Major reasons for this popularity have been: (a) a significant reduction in the cost of dyeing and printing, (b) the extreme ease of coloration, and (c) the recently improved quality of dyeing/prints (Table I). Improved color fastnesses have resulted because of recent product developments (5,6). An additional reason for pigment growth in the U. S. A. has been passage of the Toxic Substances Control Act in 1976 (7). With more and more dyes being discontinued, pigments are conveniently finding a place in U. S. dyehouses.

Pigments have little real substantivity for textiles and therefore must be held onto the fabric surface by means of binders. These binders are low molecular weight polymers and copolymers at the time of application. Upon further polymerization, they cross-link and bond to the textile fiber and to the pigment. Thus, the fastness properties of pigment paddings depend upon the success of proper curing of the binders (8). While proper curing is imperative, it can be achieved by use of an efficient catalyst at lower temperatures and shorter cure times than those conventionally employed.

Pierce and co-workers (9) developed a highly active catalyst system for easy-care finishing. Their system consisted of a metal salt with a hydroxy organic acid to produce a highly active catalyst which cured cross-linking agents rapidly under normal conditions. In fact, these catalysts are so active that good curing was achieved with lower temperatures or shorter times than usually employed in conventional resin finishing with methylol amides. This catalyst system--an equimolar mixture of magnesium chloride hexahydrate and citric acid--has been used in pigment padding and pigment printing (10,11). Only three other studies have reported the use of active catalyst systems for energy saving in pigment applications to textiles (12,13,14).

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Table I. Main Features of Pigment Padding

1. Low cost (as compared to vats and Indigosals).
2. Ease of coloration.
3. Bright shades.
4. No specialized equipment necessary.
5. High rate of production.
6. Variety of shades obtained by a simple process of mixing pigments. No problem of compatibility if the pigments of the same type are mixed.
7. Elimination of soap-offs and rinse.
8. Reproducibility.
9. Combination of dyeing and finishing operations in one bath.
10. Stripping of off shades still a problem.
11. Deep shades not possible.
12. If dyed on a tenter frame as suggested, selvages will have clip marks. (Really of little consequence as the garment industry in most cases will discard the selvages.)

The approach taken in this paper of applying technology from easy-care finishing and adapting it to pigment padding and pigment printing is the first of its type. The purpose of this paper is to describe low-energy pigment padding and pigment printing by the use of a highly active catalyst, and to outline an economical process for combining pigment dyeing with finishing in a single operation. All formulations and processes reported have been successfully employed on cotton and cotton/cellulosic fabrics by commercial textile mills in India with considerable savings in cost.

Pigment Padding With A Highly Active Catalyst

Light- and medium-depth shades are easy to obtain with pigments; however, with deeper-depth shades, streaky nonuniform paddings result. Pastel shades are obtained by using pigment concentrations up to 3.5 g/l in the pad bath and medium depths are obtained with 3.5 to 8.0 g/l of pigments, with 60-80% wet pick up. A three-bowl padder gives better uniform padding results than those obtained on a two-bowl padder. The basic steps involve padding, drying, and curing at 140-150°C. In pigment dyeing, the substrate should be thoroughly pretreated for the best padding results.

Pad bath formulations with (a) a highly active catalyst and (b) a conventional catalyst, are shown in Table II. A highly active catalyst may cause low shelf-life of the padding solution. It is, therefore, added last to the formulation to avoid premature polymerization or coagulation of the binder. A strong solution of the mixed catalyst is kept ready and the required quantity of this solution is dispensed through a measuring cylinder and added to the pad bath.

By the use of a highly active catalyst system, the costly step of curing at 140-150°C for 3 min. has been replaced by a more economical operation of mild curing on drying cans. Citric acid and magnesium chloride hexahydrate (1:1 molar ratio) provide a highly active catalyst system to fix pigment dyeings at low temperature and shorter curing times. The dyeings are mild-cured by passage over drying cans at 85-95°C in 40 to 60 seconds. This combination of time and temperature for mild curing may vary slightly from plant to plant, and conditions suitable for each individual plant are determined by checking the fastness properties of the pigment dyeings. In general, energy required for mild curing is only one-fourth of that required for conventional curing.

Fastness properties (especially wash fastness and wet- and dry-crock fastness) of the dyeings by the present method are comparable to those obtained by conventional dyeing. The merits of the present catalyst system are: (a) it does not require an afterwash, and (b) there is minimal danger of overcuring.

Table II. Pad Bath Formulations

Ingredients	With Conventional Catalyst[a]		With Highly Active Catalyst[b]	
	For Light Shade (g/l)	For Medium Shade (g/l)	For Light Shade (g/l)	For Medium Shade (g/l)
Pigment	0.0-3.5	3.5-8.0	0.0-3.5	3.5-8.0
Binder	10.0	15.0-20.0	10.0	15.0-20.0
Antimigrant (2% solution used to prevent migration)	20.0	20.0	20.0	20.0
Water (To make up the total volume to one liter)	X.0	X.0	X.0	X.0
Diammonium phosphate (30%) or Ammonium chloride (30%)	15.0	20.0	--	--
Magnesium chloride hexahydrate & citric acid	--	--	0.6 0.6	1.0 1.0

[a] Pad, dry on a padder synchronized to a float dryer and cure at 140-150°C for 3 min.

[b] Pad, dry (on a tenter frame) and cure at 85-95°C for 40-60 sec. Mild curing is done by passage through steam-heated drying cans.

[Data from Active Catalyst System for Pigment Padding (10)]

Combination With Easy-Care Finishing

With pigment dyeing it is possible to combine padding and finishing operations for easy-care finishing into a single operation through a tenter frame (Table III). The major saving results from elimination of a dyeing operation on the padder. Additional savings also result because the dyeings are carried out at a speed of 60 yds/min. on a five chamber frame instead of at 25-30 yds/min. through a padder attached to a three chamber float dryer. With highly active catalysts, the processing sequence is short and economical and the dyed goods move out of dyehouses faster.

Starch finishes are still used in India. Starch cannot be incorporated into pigment pad-bath formulations since it interferes with the final fastness requirements of pigment dyeings. By incorporating polyvinyl acetate and a softener glaze paste into pad-bath formulations, it is possible to combine padding and finishing in one operation to obtain a conventional (non-resin) finish. Compared to starch finishes, this formulation imparts increased fullness, and drape with a soft, silky hand.

Pigment Printing With A Highly Active Catalyst

Generally on roller printing runs, printing designs use pigment color depths up to 5%. For special designs and for sharp fall-on effects, higher percentages of pigment color (8-10%) are used. A typical print paste formulation using a highly active catalyst is given in Table IV. Up to 5% depths, 0.3% magnesium chloride hexahydrate and 0.3% citric acid are used. For higher depths, a greater concentration of the highly active catalyst is used. Basic steps in printing remain the same, namely, printing, predrying (on the roller printing machine), and mild curing to fix the prints.

Prints are mild cured at 95°C for 1-1.5 min. depending on the coverage and the overfalls in a design. Alternatively, prints are cured rapidly at 150°C in a polymerizer at 3 to 4 times the conventional speed. Time required for mild curing of pigment prints is greater than that required for fixing pigment dyeings. The hydrocarbon oil from prints has to be completely evaporated before total curing occurs. In the mild-curing on drying range, the width of the fabric cannot be controlled and shrinkage results. However, this shrinkage is corrected in the subsequent finishing through a tenter frame. Advantages of highly active catalyst are listed in Table V.

The printing system with the highly active catalyst works well on washable grooved rubber blanket without using backgreys. This blanket is embossed with very fine lines producing grooves that are slightly inclined towards the selvage of the blanket. These "v" shaped grooves have the capacity to hold the quantity of color struck through cloth being printed. With backgreys, the

Table III. Typical Formulations

Ingredients	Pigment Padding + Easy Care Finish Formulation (g/l)[a,b,c]	Pigment Padding + Conventional Finish Formulation (g/l)[d,e]
Pigment	0.1-8.0	0.1-8.0
Padding binder	10.0-20.0	10.0-20.0
Antimigrant (2%)	20.0	20.0
Urea-formaldehyde or Dimethylol dihydroxyethylene urea	90.0-110.0	-
Polyethylene emulsion	20.0	-
Magnesium chloride hexahydrate &	1.0	1.0
citric acid	1.0	1.0
Poly vinyl acetate	-	5.0-7.0
Stearic acid base, softener glaze paste	-	2.0-5.0
Water (To make up the total volume to one liter)	X.0	X.0

PROCEDURE: [a] Pad, dry on a tenter frame and mild-cure on drying cans.

[b] Soften the cured fabric through 10.0 g/l polyethylene solution on a tenter frame.

[c] Sanforize. [d] Pad, dry on a tenter frame and mild cure on drying cans.

[e] Calender.

Care will have to be exercised to compensate the loss in width due to width-shrinkage on a passage through drying cans.

[Data from reference 10]

Table IV. Typical Print Paste Formulation[a,b]

% (by Wt.)	Ingredients
4.0	Pigment
92.4	Emulsion thickening agent containing 8-10% binder
1.0	Urea (50%)
2.0	Gum tragacanth (6%) (Film-Forming Agent)
0.6	Highly active catalyst (solution containing 0.3% magnesium chloride hexahydrate + 0.3% citric acid)
100.0	

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[a] Print, and mild-cure by a passage through steam heated drying cans at 95°C for 1-1.5 min. Alternatively, it can be rapid cured through a polymerizer.

[b] If the conventional catalyst [2% diammonium phosphate (30%)] is used, then curing is done through a polymerizer at 150-160°C for 3-4 min.

[Data from Low Energy Curing Pigment Printing (15)]

Table V. Highly Active Catalyst in Printing

When compared with conventional catalyst (NH_4Cl), its advantages are:

1. Comparable color yield.
2. Comparable wash-fastness and wet and dry crock-fastness.
3. Excellent stability of paste with respect to time and also prolonged applied stresses on roller printing.
4. Use of left-over print paste by mixing with the newly-made print paste.
5. Savings in electrical energy.
6. Increased production.
7. Savings in labor.
8. Reduced processing cost.

system is not suitable since it will increase the consumption of backgreys as the prints are fixed on drying onto the backgreys. Extensive industrial-scale working has not revealed any serious problem with regard to running or operating processes in roller printing.

Since aqueous solutions are extremely sensitive to salts, the active catalyst system is not suitable with an all aqueous system; it is only suitable for oil-in-water system. Characteristics of oil-in-water emulsion systems have been discussed by Parikh (15).

Overdyed Pigment Prints

For overdyed pigment prints over light pigment grounds, experience has shown that the final results of either of the following procedures are almost identical: (a) pigment printing followed by pigment dyeing, or (b) pigment dyeing followed by pigment printing. The sharpness of the prints is marginally superior in the procedure of pigment printing of pigment grounds. However, procedure (b) is lengthy and its advantages outweigh its disadvantages for the procedure of pigment dyeing of pigment printed fabric. Thus, for overdyed pigment prints, bleached fabric is first printed, then transferred to a tenter frame for simultaneous dyeing and finishing. Benefits of the present technique are obvious (Table VI). The most expensive steps on the polymerizer and tenter are saved. The prints obtained by the present technique have better fastness. A high degree of fastness on prints is expected because of overpadding of additional binder from the pigment pad bath formulation.

Energy savings have been achieved in this technique without sacrificing the quality of the final product. While maintaining the quality requirements, the additional benefits have been: faster movement of goods, less stock in process, improved productivity and savings in overhead costs in dyeing and/or printing. All these benefits lead to a greater economy in cost of production in a dyehouse working.

Abstract

A highly active catalyst system (an equimolar mixture of magnesium chloride hexahydrate and citric acid) was incorporated into a pigment padding formulation in place of conventional catalysts such as diammonium phosphate or ammonium chloride and a rapid cure or mild cure was realized. This process permits mild curing on drying cans at 95-100°C for 40-60 seconds instead of the usual curing at 150°C for 3-4 minutes. The result is a significant saving in the use of energy. Another merit of the system lies in the fact that there is practically no danger of overcuring.

Table VI. Sequence of Operations of Printing Overpadded Fabrics

With Conventional Catalyst	With Active Catalyst
1. Pad pigment and dry the padded fabric (padder, float dryer)	1. Print (roller printing machine)
2. Print, dry (roller printing machine)	2. Pigment and finish (tenter frame)
3. Cure (polymerizer)	3. Mild-cure (drying range) or Rapid-cure (polymerizer)
4. Resin finish (tenter frame)	4. Sanforize
5. Cure (polymerizer)	
6. Through softener solution (tenter frame)	
7. Sanforize	

The same catalyst system was also used in the pigment print paste of an oil-in-water emulsion system. It also promotes curing with a minimum use of energy. Prints are fixed by mild curing on drying cans at 95-100°C for 1-1.5 minutes instead of conventional curing at 150-160°C for 3-4 minutes.

Pigment padding offers particularly great technical and economical advantages when combined with easy-care finishing in a single operation through a tenter frame. The most significant benefits and economic savings accrue from pigment printing of over padded pigment grounds.

Literature Cited

1. Ferguson, J., Pigments for Textile Printing, Int. Dyer, (1977), 157, 557.
2. Bille, H., Kruger, R. and Schmidt, T. G., Have Pigment Dyes a Real Chance in Dyeing?, Canadian Text. J., (1973), 90, 51.
3. Sylvia, M. R., Will Pigments Offset the Dyestuff Shortage, Am. Dyest. Rep., (1977), 66, 45.
4. Schmidt, W., Faulhaber, G., and Moore, A. J., Resin-bonded Pigment Printing and Dyeing, Rev. Progress Coloration and Related Topics, (1971), 2, 33.
5. Berlenbach, W., New Pigment Printing Techniques, Int. Dyer, (1972), 148, 693.
6. Schildo, W., New Developments in Textile Printing with Imperon Pigments, Int. Dyer, (1972), 148, 602.
7. 1977 Intersectional Technical Paper, AATCC Metropolitan Section, Toxic Substances Control Act: How Will it Affect the Textile Industry?, Text. Chem. Color., (1978), 10, 26.
8. Parikh, D. V., Pigment Printing: Application to Textiles, Am. Dyest. Rep., (1963), 52, 590.
9. Pierce, A. G., Jr. and Frick, J. G., Jr., Highly Active Catalysts for Wrinkle Resistance and Wash-Wear of Cotton Fabrics, Am. Dyest. Rep., (1968), 57, 864.
10. Parikh, D. V., Active Catalyst System for Pigment Padding, Text. Chem. Color., (1978), 10, 28.
11. Parikh, D. V., Low Energy Curing Pigment Printing by Use of a Highly Active Catalyst System, Presented at the Seminar on Special Topics in Textile Printing, at Clemson Univ., Clemson, S. C., April 4-6, 1978.

12. Modi, J. R., Palekar, A. W. and Trivedi, S. S., Catalyst Systems for Printing and Dyeing with Pigments, Text. Dyer Printer, (1976), 9, 53.

13. Smerz, O., Spieler, W., Seidel, M., and Waibel, W., Joint Fixing and Condensing of Printing Pastes or Pad Dyes and Finishing Products, W. Ger. Patent 2,616,983; Chem. Abst., (1978), 88, 8460.

14. Varghese, J., and Doshi, B. A., Sulphamic Acid and its Ammonium Salt as Catalysts for Pigment Prints, Int. Dyer, (1978), 160, 231.

15. Parikh, D. V., Low Energy Curing in Pigment Printing, Text. Chem. Color., (1978), 10, 230.

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Radiation-Curable, 100% Reactive Pigment Prints: The Effect of Paste Rheology on Print Quality

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Pigment printing is extensively used in the textile industry due to its simplicity of application. Until recently, the thickeners have been white spirit emulsions, but the air pollution and cost associated with these materials have led to the use of all aqueous thickener systems based on polyacrylic acid. Process water in textile printing is consumed in tremendous quantities. All of this water must be evaporated at the cost of energy. By various estimates, the drying of the print paste and subsequent heating to fuse and cross-link the binder requires about 3000 - 5000 BTU per pound of printed fabric. This could be reduced to less than 200 BTU per pound by switching to a radiation curing procedure.

Radiation-curable pigment printing systems are based on a liquid mixture containing only pigment and reactive chemicals that can be cured rapidly at room temperature by ultraviolet (UV) or electron beam (EB) radiation. This allows about a 90% reduction in process energy, primarily due to the elimination of water and solvents and the energy needed to evaporate them and to cure the conventional binders. The pigment is dispersed in solutions of vinyl monomers and reactive oligomers and polymerized with high intensity electrons or ultraviolet radiation. Comprehensive reviews on electron beam and ultraviolet curing and applications are available in the literature (1).

Although the basis and end result of the radiation curing process is essentially the same using either electron or ultraviolet energy, the mechanisms are quite different. This is because the energy of electrons is about 50,000 times

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greater than the ultraviolet energy. This energy is necessary to effect penetration of thick or highly filled coatings. Electron curing directly excites the entire resin portion in the coating, forming free radicals throughout the system and bringing about a complete, nearly instantaneous cure without the need for initiator or sensitizers or any post-cure step. The utilization of UV radiation as an energy source for curing involves the conversion of light energy into chemical energy. This conversion is usually accomplished by a photoinitiator, which absorbs UV light and undergoes reaction leading to the formation of free radicals. Once free radicals are formed, the polymerization takes place. The propagation is followed by termination of the free radicals. The components of polymer solution are converted to a solid cross-linked polymer film almost instantaneously, leaving a tack-free coating on the substrate (2). Several investigators (3,4,5) have studied techniques in electron beam and ultraviolet curing to produce elastomeric films with especially high extensibility suitable for textile applications. Feasibility of the radiation curing of pigment prints has been studied by Walsh *et al.*(6). The approach used was to print fabric with a mixture of reactive oligomer (polyester-urethane-acrylate), monomer, and pigment, and cure with electron beam or ultraviolet radiation. This has been used quite successfully in the commercial printing of paper, packages, and metal (7,8).

Application of radiation-curable printing pastes with conventional printing equipment results in too much binder in the printed area and fabrics that are too stiff and costly. The switch from 10% to 100% solids means that roughly one-tenth as much material should be deposited in the printed area. This problem was solved by Walsh *et al.*(6) using a laboratory batch printing technique. General objectives of this work are to print fabric continuously with radiation-curable print paste using a roller printing machine at low add-on and to obtain good print quality. This may be achieved by using print paste having optimum rheology and by choosing the proper depth of engraving. The rheology of suitable radiation curable print paste systems has been studied and is reported here. Radiation-curable, resin-bonded pigment printing pastes exhibit "plastic flow" with a "Bingham" yield stress and a constant plastic viscosity after yield. The primary effect of increasing the oligomer level in the print paste is to increase the plastic viscosity without affecting the yield stress greatly. The paste, therefore, has a lower "shear thinning" character at higher acrylo-urethane oligomer levels. Increasing the levels of Cab-O-Sil and/or pigment in the print paste does not alter the plastic viscosity, but it increases the Bingham yield stress. The paste thus has a greater "shear thinning" character at higher Cab-O-Sil or pigment levels. As the amount of the solvent in the printing system is decreased in commercial print paste systems, more polymeric thickener is added, and the behavior of the system becomes more pseudoplastic rather than Bingham-like. The specific objective of this work was to determine the optimum rheology for low add-on printing with radiation-curable print pastes. The rheological behavior of the print paste was related to the add-on and the print quality. A qualitative relationship between rheological parameters and print quality was also obtained.

Experimental

The printing was carried out using a Sauer-Essig type, laboratory roller printing machine. A special chrome-plated, copper roller was used, on which seven strips of 1.5 inch width and 0.5 to 5.5 mil depth were engraved. The machine was run at a speed of 10 yd/min. The maximum pressure that the machine could withstand was applied during printing. The printed fabrics were cured by UV. The ultraviolet light was a Linde PARS-102 laboratory/quality control unit. The doses used for UV-curing were 0, 2.1, 4.1, 10 and 40 (feet/min.)$^{-1}$ passes x 10^{-3}. These are ratios of number of passes uner the beam to line speed and are proportional to the residence time under the lamp, which is about 8 inches long and has a total intensity of 760 watts/ft^2.

In the absence of any quantitative method for assessing print quality, it was necessary to rely on subjective judgment. The sharpness and skinniness ratings were established by visually examining many printed stripes. In this manner standard sharpness and skinniness scales were made which were rated from 1 to 5, with 5 indicating excellent, 1 poor, and 2, 3, and 4 designating intermediate values. The ratings reported have an uncertainity limit of about ±0.5.

Results and Discussion

The color pastes employed in the machine printing of textiles are rheologically complex fluids. The rheological properties of these pastes are of the greatest importance in predicting their behavior in machine printing such as print sharpness, penetration, and skinniness (lack of adequate coverage, resulting in white spots in the printed area). A low viscosity, for example, results in flushing and lack of sharpness while a high viscosity causes inadequate penetration and skinniness as well as mechanical problems in printing.

As shown in Figure 1, the acrylo-urethane oligomer level in the print paste does not have a significant effect on the percent add-on at a constant depth of engraving. The yield stress increases slightly with acrylo-urethane oligomer concentration but the plastic viscosity increases significantly; this results in a lower "shear-thinning" character of the paste and thus insignificant variation in

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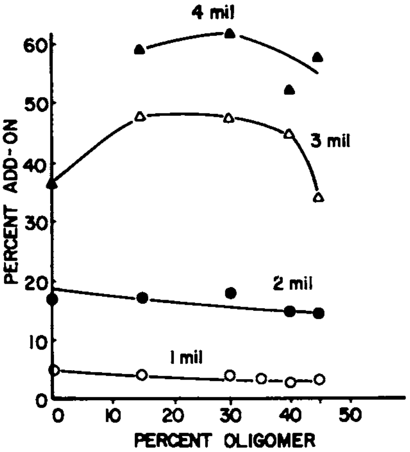

Figure 1. Effect of acrylo–urethane oligomer (MW 6000) level on percent add-on of polyester/cotton, 50/50 fabric at various depths of engraving: 2.5% Graphtol Blue 6825

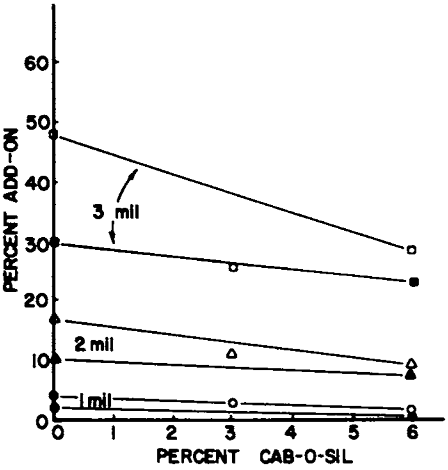

Figure 2. Effect of Cab-O-Sil level on percent add-on of fabrics at various depths of engraving: (□, △, ○) 2.5% pigment; (■, ▲, ●) 6% pigment. 15% Acrylo–urethane oligomer, Graphtol Blue 6825, P/C 50/50.

percent add-on. As expected, the percent add-on increases with the depth of engraving. Incorporation of Cab-O-Sil in the print paste decreases the percent add-on (as indicated in Figure 2), but increasing the amount of acrylo-urethane oligomer from 15% to 30% in the print paste formulations that contain Cab-O-Sil does not further alter the percent add-on significantly (Figures 2 and 3). The Bingham yield stress increases with the pigment or Cab-O-Sil level but the increase in plastic viscosity is not great. The paste, therefore, has a greater shear-thinning character which decreases to some extent the percent add-on.

This effect of rheology of the print pastes on the add-on is explained by taking an analogy from the rheology of printing inks (9). The pressman judges the rheological properties of ink by tapping out an ink film (of printing thickness) and determining its resistance to splitting. The length of ink is rated "short" or "long" according to how long a filament can be pulled out on a spatula without breaking. Ink "shortness" has been defined as the ratio of yield stress to plastic viscosity in the Bingham terminology. In the printing of paper, an ink film splitting equation has been developed to determine the amount of ink transferred from the plate to the paper surface:

$$y = b + f\,(x - b)$$

where

y is the amount of ink transferred to the paper

x is the amount of ink on the plate

b is the amount of ink immobilized during the impression (by penetration into the pores), and

f is the fraction of residual ink film split to the paper.

A correlation has been found between f and shortness. For low shear rate data on plastic viscosity and yield point, f decreases linearly with increasing shortness of the print paste, and approaches 0.5 as shortness goes to zero (9). Variation of oligomer in the print paste does not alter shortness significantly (Figure 4); hence f does not vary much, explaining the insignificant variation of percent add-on with acrylo-urethane oligomer. Addition of Cab-O-Sil to the print paste increases the yield stress and thus increases the shortness significantly, resulting in lower values of f, therefore, the percent add-on decreases. The percent add-on approaches a constant value (b) at high shortness as 'f' approximates to zero. In order to obtain higher sharpness ratings, it is essential that the print paste should have greater viscosity and fairly high yield stress. The higher yield stress helps to stop the spreading of the print paste beyond the printed area. The force which tends to spread the print paste beyond the printed area is greater at higher

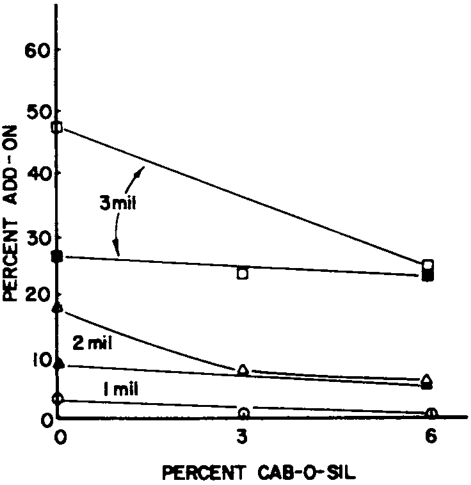

Figure 3. Effect of Cab-O-Sil level on percent add-on at various depths of engraving: (□, △, ○) 2.5% pigment; (■, ▲, ●) 6% pigment. 30% Acrylo–urethane oligomer, Graphtol Blue 6825, P/C 50/50.

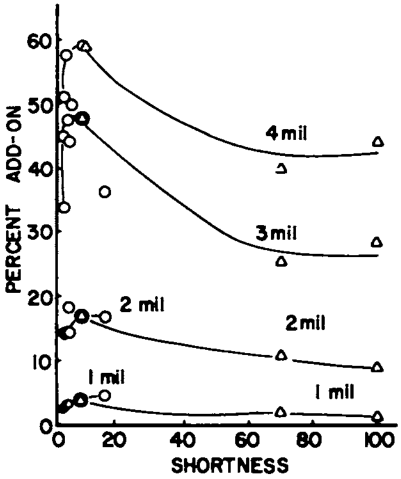

Figure 4. Effect of shortness on percent add-on at various depths of engraving: (○) oligomer variation; (△) Cab-O-Sil variation.

add-on, however, the restoring force does not vary with the percent add-on and thus results in lower sharpness ratings at higher percent add-ons (Figure 5). The sharpness ratings increase with acrylo-urethane oligomer level at the lower depths of engravings due to increase in the plastic viscosity at higher oligomer concentration (Figure 6). The lower sharpness ratings at 0.5 and 1 mil are an artifact due to lighter print shade obtained at the lower depths of engraving. These appear less sharp than they actually are, as has been shown by Becker (10) using instrumental techniques for measurement of sharpness. Addition of small amounts of Cab-O-Sil in the print paste formulation increases yield stress and apparent viscosity greatly and hence improves the sharpness ratings of the print as shown in Figure 7. Increasing the pigment level in the print paste formulation containing Cab-O-Sil does not affect the sharpness ratings of the print because they are already quite high.

For good skinniness ratings, it is necessary to have adequate fabric coverage by the print paste. The rheology of the print paste plays a vital role in achieving acceptable skinniness ratings. It is necessary that print paste should have optimum plastic viscosity, which helps in ease of flow of the print paste into the fabric at high shear rate during printing, to give better fabric coverage. The skinniness ratings increase with depth of engraving or percent add-on as shown in Figure 8. The skinniness ratings do not vary with the acrylo-urethane oligomer level at 0.5 mil and 4 mil as shown in Figure 9. At very low add-ons, the rheological properties do not affect skinniness ratings because there is not enough paste on the fabric. At 4 mil depth of engraving, the percent add-on is very high and there is ample paste independent of rheology on the fabric for full coverage. The increase in skinniness ratings at the intermediate depths of engraving is evidently due to the increase in apparent viscosity of the print paste as the oligomer level is increased. At the higher apparent viscosity, when the paste is transferred to the fabric under high tension, there is probably a greater tendency for flow of the paste in the lateral direction rather than into the yarns in a perpendicular fashion; this results in higher skinniness ratings. Skinniness is also improved by incorporating 3% Cab-O-Sil in the print paste formulations, but when the amount of Cab-O-Sil is increased to 6%, the skinniness ratings are lowered (Figure 10). The higher skinniness ratings at 3% Cab-O-Sil level is due to greater apparent viscosity. The apparent viscosity and Bingham yield value are very high when the print paste contains 6% Cab-O-Sil, resulting in poor flow of the paste in the lateral direction in the printed area and poor skinniness ratings of the print. The effect of pigment on the skinniness ratings is similar to that of Cab-O-Sil. At a constant depth of engraving, the skinniness ratings are lowered at higher pigment levels (Figure 11).

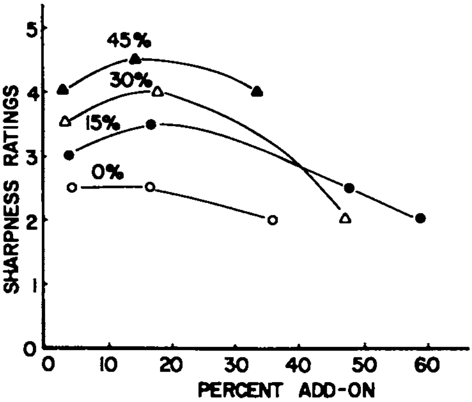

Figure 5. Effect of percent add-on sharpness ratings of polyester/cotton, 50/50 fabrics at various acrylo–urethane oligomer (MW 6000) levels: 2.5% Graphtol Blue 6825

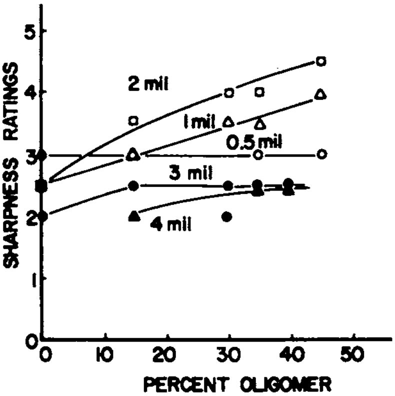

Figure 6. Effect of acrylo–urethane oligomer (MW 6000) level on sharpness ratings of polyester/cotton, 50/50 fabrics at various depths of engraving: 2.5% Graphtol Blue 6825

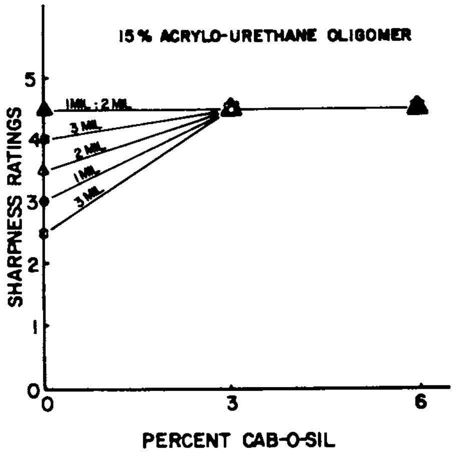

Figure 7. Effect of Cab-O-Sil level on sharpness ratings of fabrics at various depths of engraving: 15% acrylo–urethane oligomer, P/C 50/50, Graphtol Blue 6825. (■) 3 mil 6% pigment; (▲) 2 mil 6% pigment; (●) 1 mil 6% pigment; (□) 3 mil 2.5% pigment; (△) 2 mil 2.5% pigment; (○) 1 mil 2.5% pigment.

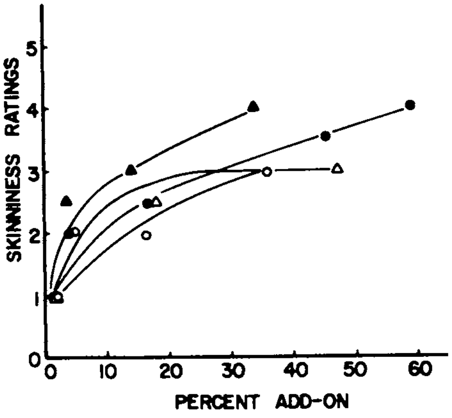

Figure 8. Effect of percent add-on on skinniness ratings of polyester/cotton, 50/50 fabrics at various acrylo–urethane oligomer (MW 6000) levels: 2.5% Graphtol Blue 6825. Oligomer: (○) 0%; (●) 15%; (△) 30%; (▲) 45%.

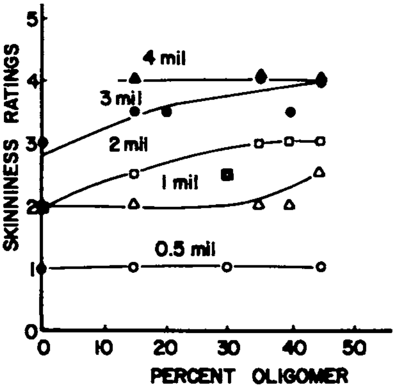

Figure 9. Effect of acrylo–urethane oligomer level on skinniness ratings of polyester/cotton, 50/50 fabrics at various depths of engraving: 2.5% Graphtol Blue 6825

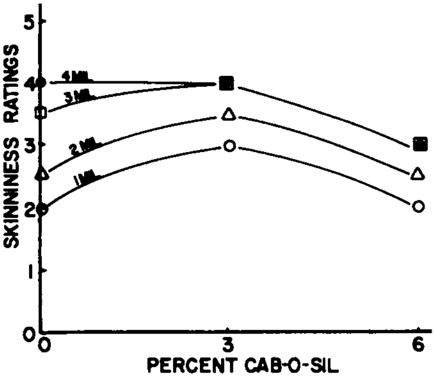

Figure 10. Effect of Cab-O-Sil level on skinniness ratings of fabrics at various depths of engraving: 15% acrylo–urethane oligomer, 2.5 Graphtol Blue 6825, P/C 50/50.

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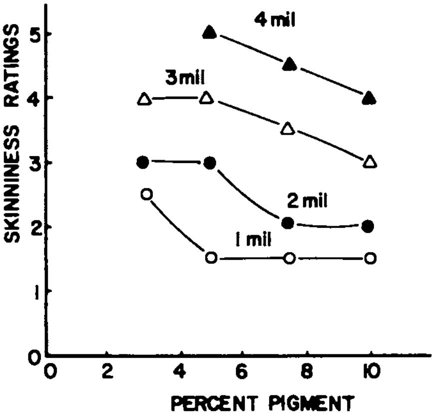

Figure 11. Effect of pigment level on skinniness ratings of polyester/cotton, 50/50 fabrics printed with radiation-curable system (2.5% Graphtol Blue 6825, 15% acrylo–urethane oligomer (MW 6000), 79% monomer mixture EP-4 (80%) and v-pyrol (20%), 3% Cab-O-Sil, and 3% vicure 10. Then required amount of pigment was added.

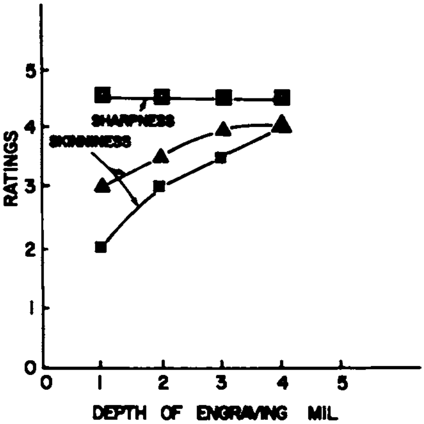

Figure 12. Comparison of print quality (sharpness and skinniness ratings) of polyester/cotton, 50/50 fabrics printed with radiation-curable system (2.5% Graphthol Blue 6825, 15% acrylo–urethane oligomer (MW 6000), 79.5% monomer mixture and 3% Cab-O-Sil) and all aqueous systems: (■) Skinniness rating—all aqueous system, Lumatex Blue BGT; (▲) skinniness rating—radiation-curable system; (△) sharpness rating—radiation-curable system; (□) sharpness ratings—all aqueous system Lumatex Blue BGT.

The print quality of polyester/cotton, 50/50 fabrics printed with the radiation-curable system is very close to that using an all aqueous system (Figure 12) and presumably due to their similar rheological behavior.

Summary and Conclusions

In conventional pigment printing of textiles, weight gains in the printed area (after drying) of about 10% are common. In order to realize the large energy savings associated with radiation curing, the printing must be accomplished without water or solvent. It has been shown that this can be achieved with roller printing of 100% solids systems by lowering the depth of engraving to about 2 mils and reducing the paste transfer by increasing the yield stress (and ink shortness). Print sharpness and color coverage were optimized by adjustments in the paste rheology. Prints with more than adequate sharpness were achieved by adjustments in paste rheology but the best skinniness ratings achievable (about 3.5) are still less than acceptable (about 5). The best commercial aqueous print paste gave slightly lower skinniness ratings (about 3.0) under similar conditions indicating that the low add-on, not the high percent solids, is responsible for the low skinniness ratings. Recent preliminary experiments have shown improvements in color coverage by increasing the engraving density, or the lines per inch, but it is not likely that this will suffice for heavier, less even fabrics. Foaming the paste to increase its volume is currently under study and the results look quite interesting. This technique, which essentially substitutes air for water or solvent, will be reported on at a later date.

References

1. Schroeter, S. H., "Radiation Curing of Coatings," Ann. Rev. Mater. Sci., (1975) 5, 115.

2. McGinniss, V. C., "Photoinitiator of Acrylate Systems for UV Curing," 3rd International Radiation Curing Conference, Proc. of SME Radiation Curing Conference, FC76-486 (1976).

3. Oraby, W., and Walsh, W. K., "Elastomeric Electron Beam Cured Coatings: Structure-Property Relationships. Part I. Oligomer Structure," J. Appl. Polym. Sci., in press.

4. Oraby, W., and Walsh, W. K., "Elastomeric Electron Beam Cured Coatings: Structure-Property Relationships. Part II," J. Appl. Polym. Sci, in press.

5. Morgan, C. R., Magmotta, F., and Ketley, A. D., "Thiol/Ene Photocurable Polymers," J. Polym. Sci., Polym. Chem. Ed., (1977) 15, (3), 627.

6. Walsh, W. K., Makati, A., and Edison Bittencourt, "Radiation Curable, 100% Reactive Pigment Prints," Proc. AATCC Printing Symposium, "Meeting the Challenge of the '80's," New York City, January 1978.

7. Carter, R. G., "Formulating Trade-Offs in Developing Low Viscosity Photocurable Coatings for Packaging," Proc. of SME Radiation Curing Conference, FC76-533, (1976).

8. Hamilton, R. C., "U.V. Printing on Two Piece Aluminum Cans," Proc. of SME Radiation Curing Conference, FC76-506, (1976).

9. Eirich, F. R., "Rheology Theory and Practice," Vol. 3, Academic Press, New York and London, 1960, p.195.

10. Becker, C. L., "Microscopical Investigation of Print Quality of Radiation Curable Pigment Printing," M.S. Thesis, North Carolina State University, Raleigh, N.C., 1978.

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Dyebath and Auxiliary Bath Reuse for Energy and Mass Conservation

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The textile industry uses approximately 125 billion gallons of water annually (1). Much of the process water is discharged with appreciable quantities of organic and inorganic chemicals (dyes, pH control agents, lubricants, surfactants, auxiliaries, oligomers, etc.) which require extensive treatment of the wastewater and which contribute to the pollution problems associated with textile processing. In the past, the textile pollution problem has been attacked by construction of waste treatment facilities. As requirements became more stringent, the waste treatment plant was expanded or additional treatment processes were added to meet the standards. The mushroom approach has consumed large sums of non-income-producing capital and has increased the operating costs of many textile plants.

In addition to problems associated with water supply and pollution control, the increasing cost and decreasing supply of energy represents a major problem for the textile industry. Energy requirements for the United States textile industry in 1971 (most recent comprehensive data) were equal to approximately 6/ million barrels of oil (2). Industry is heavily dependent on petroleum products and natural gas (the fuel currently in shortest supply) for a major part of process energy requirements. If the industry is to adapt to the shortages or curtailments of energy, new processes or process modifications must be implemented on a broad, industry-wide scale.

Two basic types of procedures are used for textile coloration -- pad-fix (continuous) processes and exhaust (batch) processes. Continuous dyeing is used primarily for long runs of a given fabric style. Because of their continuous nature and the use of relatively smally volumes of dye liquor, these processes tend to be more efficient than batch processes. Exhaust batch processes are generally very inefficient in their use of chemicals, water and energy and generate large volumes of wastewater that must be treated. Despite these disadvantages, the versatility, ease of control, and short-run capability of exhaust processes enhance their desirability for coloration of many textile products.

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A number of different types of batch dyeing processes (beck dyeing, jet dyeing, jig dyeing, package dyeing, beam dyeing) are used in the textile industry. Batch processes were used for dyeing an estimated five billion pounds of textile fibers and fabrics in 1973 (3). Batch processes readily lend themselves to process modifications which can reduce energy and material requirements for dyeing. Reuse of dyebaths and auxiliary baths for processing numerous batches of material was thus a logical area of research for system modification.

Development of the Reuse System

In a conventional batch dyeing process the machine is filled with water, the goods to be dyed are entered, and the fabric moved through a bath (or a bath moved through the goods) to saturate the material with water. Chemical auxiliaries such as wetting agents, pH control agents, leveling agents, and chelating agents are then added to the bath followed by the dyes. The machine is heated from ambient to dyeing temperatures at a fixed rate (usually 3 - 4°F/min.) and held at the dyeing temperature for the time required to complete the dyeing. The goods being dyed are check for proper shade, and if the shade has been attained, the dyebath is discharged to the drain. The goods are then post-scoured and/or rinsed to remove unfixed dye. The goods are removed from the machine, and the machine is refilled with water for the next load.

If the dyebath is examined before and after the dyeing cycle, two major changes have occurred: most of the dye has been removed from the bath by the yarn or fabric, and the bath is hot rather than cold. Most of the auxiliary chemicals added to the bath are still present in the same condition as they were at the start of the dyeing cycle. When the dyebath is discharged to the drain, large quantities of energy, water and useful chemicals are lost. A more reasonable procedure would be to analyze the spent dyebath for the remaining dye, to reconstitute the bath to the desired strength, and to reuse it for subsequent dyeings. Reuse of dyebaths was calculated to significantly reduce the energy, water and chemical requirements in batch dyeing, as well as reduce pollution loads.

A number of technical problems required solution before dyebath reuse could be broadly applied in batch dyeing. An analytical system had to be developed to simply, accurately, and economically determine the concentration of dyes remaining in the bath. The analytical technique had to be compatible with existing dyehouse personnel, space, time and equipment constraints. Dyeings had to be started at elevated temperatures (170° F). However, the increased rate of dye adsorption from the bath at these temperatures could potentially result in spotting and poor levelness in the recycle dyeings. Materials handling procedures had to be worked out to give scouring, dyeing, and rinsing cycles compatible with current plant operation procedures. Evaluation procedures were also required to insure that dyeings in recycled dyebaths were equivalent in quality to conventionally-dyed products.

In addition to the dyebath, several auxiliary baths are used in batch textile processing to clean dyed goods and/or to fix the dye to the fiber. Considerable energy, water and chemicals are also wasted when these auxiliary baths are drained to the sewer. Plant pollution problems are also worsened by the additional effluent. Virtually all of the chemicals used in the auxiliary baths (sodium hydrosulfite and hydroxide, surfactants, etc.) are colorless, and thus do not lend themselves to simple spectrophotometric analysis. The chemicals are usually present in considerable excess, however, and are not exhausted or destroyed in the process. Theory suggested, therefore, that particular baths other than the dyebath could be reused to post-treat a number of material batches without detailed and precise quantitative analysis.

Analysis System for Dyebaths. The strong absorption of dyes in the visible region of the spectrum provides the simplest and most precise method for determination of dye concentrations. The absorbance, A, of a dye solution can be related to the concentration by the modified Lambert-Beer equation (4):

$$A = \log I_0/I = Kc$$

where I is the intensity of the visible radiation falling on the sample, K is a constant including the path length of radiation through the sample and a constant related to the absorptivity of the sample at a given wavelength and c is the concentration of the absorbing species. In mixtures of absorbing species, the absorbance at any wavelength is the sum of the absorbances of each absorbing species and is given by:

$$A = K_1c_1 + K_2c_2 + K_3c_3 \dots + K_nc_n$$

This characteristic of light absorption by dyes is important in the analysis of dye mixtures of the type found in spent dyebaths. For such dye mixtures, the absorbance can be measured at a number of wavelengths and the concentration of the dyes determined by simultaneous solution of a set of linear equations of the type shown above. The wavelengths selected for the analysis are generally those for which one of the dyes gives a maximum absorbance.

A second procedure for obtaining dye concentrations from absorbance data was developed for very complex dye mixtures. In this procedure the absorbance of the spent dyebath was measured at 16 equally-spaced wavelengths from 400 to 700 nm. The dye concentrations were determined from a least-squares fit of the absorbance curve at these 16 wavelengths. A computer program in FORTRAN IV was developed to determine the concentrations of up to six dyes in a mixture by the sixteen-point technique.

The Lambert-Beer relationship is generally invalid for absorbing species that are not in solution. Most dye classes used in the dyebath reuse research (acid, basic, direct, reactive) are soluble in the dyebath and the spectrophotometric analysis could be carried out directly on the dyebath. Disperse dyes, however, are not water soluble and required development of new techniques to give true dye solutions. The spent disperse dyebath sample was placed in a separatory funnel, a measured quantity of an organic solvent (benzene or toluene) was added and the mixture shaken to extract the dye into the organic layer. The spectrophotometric analysis was then conducted on the dissolved dye in the organic layer. Standards for calculation of the $\underline{K}$ values for disperse dyes were treated in the same way to insure accuracy of the procedure.

Correction for absorbance of species other than dyes (background absorbance) was also required in some cases. For dyebaths containing disperse dyes and using organic solvent extraction, background absorbance presented no problem. The absorbing species other than dyes remained in the water phase. For dyes measured directly in the dyebath, a correction procedure was necessary. Samples of the textile product being dyed were treated in a "blank" bath (a bath containing all chemicals except the dyes) in exactly the same way that the yarn or fabric would be dyed. Samples of the "blank" dyebath were then used to obtain standard absorption data, if present, for the blank dyebath and background $\underline{K}$ values were calculated in the same way as described above for dye. Thus, a dyebath with three dyes would be treated as if it contained four dyes with the fourth dye being the background absorbance.

A further advantage of spectrophotometers is the ready availability of a number of low-cost instruments with sufficient accuracy and reproductivity for dyebath analysis. Much of the work in the current study was carried out on a single-beam grating spectrophotometer costing approximately $2,000. The computations necessary in the analysis can be conveniently carried out on low-cost desk calculators or microprocessors. The calculations necessary for a four-dye mixture (or three dyes plus background) can be handled on a system costing less than $1,000. The least-squares fit of 16 points of the absorption spectrum can be carried out on a $3,000 minicomputer. Development of these low-cost instrument-minicomputer systems is largely responsible for consideration of dyebath reuse as a practical reality for the textile industry.

Accurate analysis for dyebath components other than dyes has not been required. Dyebath additives generally control the dyeing environment and are not consumed or removed during the dyeing cycle to any extent. In general, the auxiliary components were added to the reused baths in direct proportion to the quantity of make-up water required to replace that lost to the goods and during manipulation of the bath. For example, if 20% of the dyebath was lost during the dyeing step (primarily due to removal with the wet goods) then 20% of the original quantities of pH control agents, wetting agents, etc., was added to the bath after replacing the lost volume with fresh water.

Evaluation Producedures. Three important characteristics of textile products dyed by the reuse procedure were measured to determine if the dyeings were of acceptable quality--the uniformity, the reproducibility and the stability or "fastness".

The uniformity was assessed by selecting representative samples from the dyed lot and determining the color (tristimulus values) on a standard colorimeter (DIANO/LSCE Automate System). The difference in color of each specimen from the average color of all specimens was determined using the FMC II color difference formula (5). In this system one unit of color difference is defined as the minimum perceptible difference in color. Thus spots or unlevel dyeing could be readily identified by variations in color difference between specimens from the same dyeing.

Reproducibility of the dyeings was determined by calculation of the color differences between dyed lots and a standard dyeing of the same shade. In this calculation the color difference was determined from average tristimulus values of each dyed lot compared to a conventional dyeing, again using the FMC II equation. In addition to instrumental measurements, samples dyed by the reuse procedure were examined visually by expert dyers to further assess the color uniformity and color reproducibility.

Dyed samples were also evaluated for resistance to color changes by rubbing (crockfastness), exposure to light (lightfastness) and exposure to water (wet-fastness). Standard test methods recommended by the American Association of Textile Chemists and Colorists were used in the fastness evaluations.

Applications of the Reuse System

Carpet Dyeing. Initial studies of dyebath reuse were carried out on carpet samples. Preliminary bench-scale studies to evaluate the technical feasibility of dyeing in spent baths and to develop the required analytical techniques were carried out as part of a previously reported (6,7) research program. The current research was undertaken to scale-up the dyebath reuse system for carpet dyeing. All dyeings were carried out in a four-foot beck capable of dyeing 30 to 40 lb carpet samples. The four-foot beck is normally used in a carpet dyehouse for development work, and thus represented a reasonable pilot-scale system. Two of the carpet experimental trials--dyeing of nylon carpet with disperse dyes and dyeing of polyester carpet with disperse dyes--are reported.

Dyeing of Nylon Carpet with Disperse Dyes. The objective of the first trial in the pilot-scale experiments was to dye nylon carpet to the same shade five times with reuse of the dyebath (8). The carpet was tufted from Nylon 6 face yarn with a polypropylene primary backing. Both regular nylon and cationic-dyeable yarns were used in the carpet; however, the two types of yarns dyed to essentially the same color with disperse dyes. The carpet surface contained both cut pile and loops.

Approximately 35 pounds of prescoured carpet were placed in the standard pilot-scale four-foot beck, cold water was added to give a liquor ratio of 25:1 (approximately 100 gallons) and the auxiliary chemicals (leveling agent, 1% over weight of fabric (owf); complexing agent, 0.5% owf; pH control agent, 1% owf) were added over a fifteen-minute period. The bath was brought to the boil at 3°F/min. with direct steam injection and held at the boil for 45 minutes. The carpet was removed by hand at 200°F and rinsed three times in a separate machine. The water volume that was removed by the carpet and by evaporation (23 gallons) was added to the remaining bath, and only auxiliary chemicals calculated to bring the added water to the initial concentration were added. The residual dye concentrations were determined using the analytical procedure detailed above. A second batch of carpet was placed in the beck after bringing the bath back to 175 ° F. The dyestuffs were added to the beck over a fifteen-minute period at 175°F, the bath was brought to the boil at 3°F /min. and the cycle continued as in the first run. The reuse sequence was repeated three additional runs to give a total of five dyed batches from the same bath.

The dyed nylon batches were evaluated by color measurement and color difference calculations using the described procedure. Ten random samples were cut from each of the five nylon carpet sections (3' x 38') dyed in the reuse sequence. Color differences between the samples from the four reuse runs and samples for the initial (conventional) dyeings were calculated. The tristimulus values X, Y, and Z were obtained on the Diano instrument by measuring each sample three times against a white tile standard for a total of 30 color measurements for each carpet length. The tristimulus values were utilized with the FMC II equation to determine the end-to-end shade variation of the carpets by averaging the tristimulus values from the 30 measurements and calculating color differences in MacAdam units between the individual sample positions and the average. The averages of the tristimulus values for all 30 measurements of each carpet section were calculated, and the color difference between those averages and the average tristimulus values for the conventionally-dyed standard were calculated in order to determine overall lot-to-lot variation.

Color differences between each of 10 individual measurements along the carpet sample and the average for the sample for each of the pilot-scale dyeings are shown in Table I (8). The data demonstrated quantitatively that there was little difference in end-to-end color variation between the sample dyed in the conventional manner (Run I) and samples dyed in recycled dyebaths (Runs II to V).

Reproducibility of dyes in the recycled baths is shown in Table II. The differences in color between the first run (conventional dyeing) and dyeings in the recycled baths were determined from the difference in the average color of each run and the average for Run I. The differences in color for samples dyed in recycled baths were well within the acceptable commercial color range based on statistical measurements made on plant production samples.

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ACS Symposium Series; American Chemical Society: Washington, DC, 1979.

Table I. End-to-End Color Differences in MacAdam Units of Nylon Carpet Dyed with Disperse Dyes (8)

Position	Run I	Run II	Run III	Run IV	Run V
1	1.68	0.76	2.61	1.81	0.63
2	0.67	1.33	4.02	5.16	0.40
3	1.04	3.90	0.97	3.17	1.30
4	1.99	1.82	1.00	1.90	1.13
5	0.35	3.57	3.75	1.61	2.14
6	1.60	2.38	3.15	2.11	0.69
7	0.72	3.21	1.41	0.76	0.46
8	3.39	0.84	4.17	1.55	1.79
9	0.98	2.53	1.96	3.59	2.09
10	1.10	5.78	1.23	1.52	1.64

Textile Chemist and Colorist

Table II. Lot-to-Lot Color Differences of Nylon Carpet Dyed with Disperse Dyes (8)

Run	Color Differece Versus Control (MacAdam Units)
I (Control)	---
II	1.3
III	0.4
IV	0.5
V	0.5

Textile Chemist and Colorist

Dyeing of Polyester Carpet with Disperse Dyes. The second trial run was conducted on polyester carpet dyed with disperse dyes. In this series three shades in a color line--a light beige, a medium blue and a rust--were selected for dyeing. The chosen colors were actual large-volume shades current being marketed by a leading carpet firm. The objective was to dye polyester carpet seven times (three beige, two blue, two rust) from the same dyebath utilizing the reuse technology on the four-foot beck. In addition, the sequence was carried out using material handling procedures that were designed to be compatible with in-plant dyeing. The following procedure was used:

(1) Dye a beige carpet in conventional manner,
(2) Pump dyebath to holding tank,
(3) Rinse carpet *1* in beck
(4) Remove carpet *1* from beck
(5) Clean fiber from rinse water
(6) Enter carpet *2* for prescour
(7) Drop rinse-prescour water
(8) Pump dyebath to beck
(9) Dye carpet *2* beige
(10) Repeat steps 2 through 9 for subsequent batches.

The dyebeck was modified by the addition of a pump and an insulated holding tank for the polyester series. The final rinse bath was also used at ambient temperature and volume to give the subsequent carpet a short prescour before dropping the rinse bath.

In a typical reuse dyeing, the beck was full at the beginning of the cycle with the final rinse from the previous run (at 160° F). the carpet was entered and allowed to run for five minutes to partially remove fiber oils and identification tints. The rinse prescour bath was then dropped to the sewer and the dyebath used for coloration of the previous carpet pumped to the beck from the holding tank. The dyebath temperature on return was approximately 20:1 liquor ratio. The quantities of all auxiliaries (except carrier) were determined from the volume of fresh water added to the beck. The carpet was run for five minutes, the pH adjusted to 5.0-5.2, and the required quantities of dyes added to the bath over a fifteen-minute period. The carrier (10% owf) was then added slowly over a fifteen-minute period. The dyebath was raised to the boil at 6° F/min. and run at the boil for one hr. At the end of the dyeing the bath was returned to the holding tank and analyzed for residual concentrations. The dyed carpet was post-scoured, rinsed, removed from the beck, and air dried.

Initial inspection of the dyed carpet suggested that good color reproducibility and uniformity had been achieved. Ten samples were cut from each of the dyed samples and the color measured on the Diano Colorimeter. Each sample was measured three times to average variations due to instrument changes and sample texture differences. Tristimulus values (X,Y,Z) were calculated from the average of the three measurements.

The base color of each dyed sample was determined by averaging the ten values obtained form the samples cut from each carpet. Color uniformity was evaluated by calculation of the color difference of each of the samples from the average value for the carpet. These results for the seven dyed carpets are detailed in Table III. The color difference values were calculated using the FMC II color difference equation.

Color differences between the beck-dyed samples and standards prepared in beaker dyeings by conventional dyeing procedures have also been determined. In these calculations the average color for each carpet was determined from 10 measurements, and the difference of this average from the average of 10 measurements on the standard was determined. The calculations give a measure of the reproducibility of the dyeings in the recycled baths (Table IV). In addition to the usual FMC II color differences, the color differences in the C.I.E. 1976 recommended color space, L*a*b*, are shown for comparison. With the exception of the two blue samples, the reproducibility was excellent. Reproducibility in the blue samples was at the outer limit of what can be considered acceptable commercial carpet dyeing. A comparison of the two blue samples with each other showed that they were very close together in color ($\Delta e = 1.44$), but different from the standard. In both blue carpets the yellow was higher than the standard, and the samples were lighter than the standard. Addition of a small quantity of blue dye would have corrected this color difference between the samples and the standard. Since a "no add" policy was followed in this series of dyes, no dye add was made. A slight modification of the dye formula would have also corrected the small difference between the blue samples and the standard.

In addition to instrumental color measurements, the dyed carpets have been examined visually by four experienced carpet dyehouse supervisors. All four agreed that both the nylon and polyester carpet dyeings were acceptable as first-quality in both color uniformity and color reproducibility.

Measurement of the fastness properties of the dyeings to light, crocking and water were also carried out. These results are shown in Tables V, VI and VII. All of the dyeings exhibited commercially-acceptable fastness properties.

Economic Evaluation of Carpet Dyeing with Dyebath Reuse. The energy, materials and cost savings that are possible with reuse of the dyebath are dependent on a number of factors, including the type of yarns, the shade being dyed, the number of times the bath is used, the type of auxiliary chemicals used, and the temperature of incoming water. All of these factors will influence the possible reduction in materials, energy and cost on reuse incorporation. Calculations of these savings have been carried out based on the two reported pilot-scale dyeings of carpet, and are shown in Table VIII. The reductions in dye chemical and water requirements with recycle of the dyebath were determined directly from the measured quantities

Table III. Color Uniformity in Polyester Carpet Dyeings with Dyebath Reuse

	Δe in FMC II Units						
Sample Number	Beige #1	Beige #2	Beige #3	Blue #1	Blue #2	Rust #1	Rust #2
1	1.14	1.93	1.97	1.15	2.37	1.16	1.54
2	2.97	2.58	0.97	1.00	0.93	1.51	0.81
3	3.30	0.95	0.87	1.27	0.28	1.00	2.86
4	0.99	3.40	0.99	0.64	0.89	0.76	1.23
5	0.89	1.89	1.26	0.96	1.09	1.42	2.68
6	4.28	1.44	1.70	2.46	1.29	0.53	0.47
7	0.66	0.85	1.27	2.56	0.94	2.77	0.81
8	3.03	0.93	1.73	2.02	1.23	1.39	2.03
9	4.59	1.81	1.33	0.76	1.24	0.89	1.82
10	4.49	1.64	0.74	2.33	2.82	2.92	1.44

Table IV. Color Reproducibility in Polyester Carpet Dyeings with Dyebath Reuse

Sample	FMC II Δe	CIE L*a*b* Δe
Beige #1	0.44	1.22
Beige #2	0.76	0.43
Beige #3	0.27	0.09
Blue #1	4.85	3.64
Blue #2	3.74	2.50
Rust #1	1.70	1.17
Rust #2	1.80	1.25

Table V. Evaluation of Light Fastness for Polyester Carpet Dyed by the Reconstituted Dyebath Method

Color	Dyeing	24 hr.	48 hr.	72 hr.	96 hr.	120 hr.
Beige	1	5	5	5	4-5	4-5
Beige	2	5	5	5	4-5	4-5
Beige	3	5	5	5	4-5	---
Blue	4	5	5	5	5	4-5
Blue	5	5	5	5	4-5	4-5
Rust	6	5	5	5	5	5
Rust	7	5	5	5	5	5

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Table VI. Evaluation of Fastness to Dry Crock for Polyester Carpets Dyed by the Reconstituted Dyebath Method

Shade	Dyeing Number	Rating	
		Sample #1	Sample #2
Beige	1	5	5
Beige	2	5	5
Beige	3	5	5
Blue	4	5	5
Blue	5	5	5
Rust	6	5	5
Rust	7	4-5	4-5

Table VII. Evaluation of Fastness to Water for Polyester Carpets Dyed by the Reconstituted Dyebath Method

Shade	Dyeing No.	Rating
Beige	1	5
Beige	2	5
Beige	3	5
Blue	4	5
Blue	5	5
Rust	6	5
Rust	7	4-5

Table VIII. Reduction in Materials, Energy, and Cost by Reuse of Dyebaths in Carpet Dyeing

	Reduction in %	
	Nylon, Disperse Dyes 5 Cycles	Polyester, Disperse Dyes 7 Cycles
Dyes	3	7
Chemicals	65	7
Water	34	39
Energy	27	27
Cost	27	12

Cost Summaries for Carpet Dyeing

	Nylon, Disperse Dyes 5 Cycles		Polyester, Disperse Dyes 7 Cycles	
	Conventional	Reuse	Conventional	Reuse
Dyes (Cost/Run)	\$2.18	\$2.11	\$10.25	\$ 9.70
Chemicals (Cost/Run)	1.35	0.47	7.29	6.57
Water (Cost/Run @45¢/1000 gal)	0.45	0.29	0.26	0.07
Energy (Cost/Run @ \$3/10^6 BTU)	3.99	2.91	5.43	3.74
Total Cost:	\$7.97	\$5.78	\$22.93	\$20.08
Cost Per #:	0.046	0.033	0.094	0.082
Savings %:	27.5		12.4	
Savings ¢/#:	1.3		1.2	

used in the pilot-scale dyeings. Since the beck used was not equipped with energy monitoring devices, the energy reductions were calculated. An example of the energy reduction calculations are given in Table IX. The results confirmed that significant reductions in water use and resulting effluent volume, chemical requirements, energy requirements and cost can be achieved by dyeing carpet with reconstitution and recycle of the dyebath.

The estimated cost for a medium size (ten beck) carpet mill to convert 50% of dyeing capacity to the dyebath reuse system is shown in Table X. The calculation assumes the purchase of new equipment with a separate holding tank and pumping system for each of the five becks. At an estimated savings of one cent per pound of carpet dyed (considerably less than indicated in the Table VIII cost analysis and therefore conservative) the recovery of capital investment is still less than one year.

Batch Dyeing of Nylon Pantyhose.

Pilot-Scale Investigation. Hosiery is colored exclusively by batch dyeing processes. The two main types of equipment utilized are the overhead paddle machine and the rotating drum machine. In hosiery dyeing a limited range of dyes and auxiliaries are employed due to a narrow shade range. Thus hosiery dyeing presented an excellent opportunity for application of the reuse dyeing technology.

In the first series of reuse dyeings, Nylon 66 pantyhose was colored exclusively with disperse dyes in a two-foot Smith rotary drum machine of eight-pound capacity. A liquor ratio (wt. of water: wt. of goods) of 23:1 was utilized. Three commercial shades were dyed, consisting of light, medium and dark shades of brown. All of the shades were derived from the same three disperse dyes. A total of 10 batches of pantyhose were dyed from the same bath. The dyeing procedure and the experimental results have been reported elsewhere (8). The lot-to-lot color differences for the batches by the FMC II color program are detailed in Table XI. the data quantitatively demonstrated that the shades on the reuse runs were within the color tolerance range (three to seven MacAdam units) determined for the participating plant. The hosiery dyed in the pilot-scale reuse sequence was returned to the company, and was judged "first quality" and sold through normal channels.

Pilot-scale hosiery dyeing research was continued with some modifications from the initial sequence. Dyeings were conducted to exactly simulate the procedure formulated by the investigators and the participating company for in-plant dyebath reuse. The procedure, detailed in Table XII, differed in several respects from the one-cycle procedure utilized by the company (Table XIII). At this stage, the firm lowered the holding temperature in the hosiery dyeings from 200 to 170°F, and this change was incorporated in the revised reuse procedure. The finish bath for the dyed hosiery in the modified procedure was also utilized without alteration as a prescour bath for the subse-

Table IX. Energy Savings for Pilot-Scale Dyeings: Nylon with Disperse Dyes (5 Cycles)

Basis: 35# Carpet Samples, 875# Water (105 gal) 25:1 Liquor Ratio
Incoming Water at 60°F
Make-up Water Required Each Cycle 25 gal.
Dyeing Temperature 212°F, Rinse Temperature 120°F
Efficiency of Energy Utilization at Beck 90%
Reuse Entry Temperature 170°F
Steam Required to Hold at Boil 1#gal/hr.
Carpet Retains 300% Water Between Processes

Conventional Dyeing

Heat Bath 60° - 212°F (152° x 875# x 1.11 x 1 BTU/#) = 14.76 x 10^4 BTU

Heat Carpet 60° - 212°F (152° x 35# x 1.11 x 0.5 BTU/#) = 0.30 x 10^4 BTU

Hold at Boil for 45 min. (105 gal x 1000 BTU/lb. x 0.75 Hr) = 7.88 x 10^4 BTU

Rinse at 120°F (60° x 770# x 1.11 - [140# x 92° + 35# x 92° x 0.5]= 3.68 x 10^4 BTU

Total Per Cycle = 26.62 x 10^4 BTU
Total 5 Cycles = 1.33 x 10^6 BTU
BTU/Pound Carpet = 7,6000

Reuse Dyeing

Heat Make-up Water 60° - 170°F (1100 x 100# x 1.11 x 1 BTU) = 1.22 x 10^4 BTU

Heat Retained Prescour Water 120° - 170°F (50° x 100# x 1.11 x 1 BTU) = 0.56 x 10^4 BTU

Heat Bath 170° - 212°F (42° x 875# x 1.11 x 1 BTU/#) = 4.08 x 10^4 BTU

Heat Carpet 120° - 212°F (92° x 35# x 1.11 x 0.5 BTU/#) = 0.18 x 10^4 BTU

Hold at Boil 45 min. (105 gal x 1000 BTU/gal x 0.75 Hr) = 7.88 x 10^4 BTU

Rinse at 120°F (60° x 770# x 1.11 -[140# x 92° + 35# x 92° x 0.5]) = 3.68 x 10^4 BTU

Total Reuse Cycle = 17.60 x 10^4 BTU
Total Cycles (1 Conventional + 4 Reuse) = 0.97 x 10^6 BTU
BTU/Pound Carpet Dyed = 5,543

Energy Savings: 2,057 BTU/lb Carpet Dyed (27%)

In Energy Conservation in Textile and Polymer Processing; Vigo, T., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 1979.

Table X. Payback on Capital Costs for Carpet Dyebath Reuse

Basis:	Plant with 10 becks-- 5 to be modified for reuse Capacity 2,000 lb. per cycle, 6 cycles per day per beck No additional personnel required Savings using dyebath reuse, 1¢ per lb. of carpet dyed No productivity increases are assumed		
Capital Costs:	Hold tanks (new)	\$20,000 ea. x 5	\$100,000
	Pumps	3,000 ea. x 5	15,000
	Piping, valves	1,500 ea. x 5	7,500
	Analysis Equipment		7,000
		Total Cost:	\$129,500
Returns:	Production 5 Becks x 2000#/Beck x 6 Cycles/Day	=	60,000#/Day
	Returns Per Day 60,000#/Day x 1¢/#	=	\$600/Day
Payout:	\$129,500/\$600	=	216 Days

Table XI. Lot-to-Lot Color Differences of Nylon Pantyhose Dyed With Disperse Dyes (8)

Run	Shade	Color Difference Versus Standard (MacAdam Units)
I (Conventional)	Light	4.36
II	Light	6.15
III	Light	--
IV	Light	6.35
V	Medium	2.53
VI	Medium	3.30
VII	Dark	4.06
VIII	Dark	4.48
IX	Light	6.04
X	Light	5.64
Medium Limit[a]	Medium	7.78
Dark Limit[a]	Dark	2.89

[a] Hosiery samples supplied by the participating company and termed "just passable as first quality" by plant personnel.

Textile Chemist and Colorist

Table XII. Modified Procedure for Dyebath Reuse Pantyhose Operations

		Time (min.)
I.	Dyeing Batch I	
1.	Load machine	3
2.	Fill with cold water, raise to 90°F	7
3.	Add auxiliary chemicals, run 10 min.	10
4.	Add dyes	1
5.	Raise temperature at ca. 3°F/min. to 170°F	45
6.	Run 20 min. at 170°F	20
7.	Sample; make add if necessary	10
8.	Dump the bath to holding tank when correct shade is obtained	3
II.	Finishing Batch I	
9.	Refill with cold water	3
10.	Inject steam rapidly to achieve 110°F	4
11.	Add finish chemical and run 10 min. at 110°F	10
12.	Unload the pantyhose	3
	Cycle I Total:	119 min.
III.	Dyeing Batch II	
1.	Load machine	3
2.	Add prescour chemical to exhausted finish batch at ambient temperature	10
3.	Dump prescour bath to drain	3
4.	Refill with the analyzed dyebath from holding tank at ca. 150°F	3
5.	Add the necessary auxiliaries to reconstitute the bath over 10 min.	10
6.	Add the necessary dyes to reconstitute the bath slowly over a 10 min. period	11
7.	Raise temperature at ca. 3°F/min. to 170°F	20
8.	Run 20 min. at 170°F	20
9.	Sample; make add if necessary	10
10.	Dump the bath to holding tank when correct shade is obtained	3

Table XII. (cont'd.)

Cycle II Total:	103 min.
Total Time, Cycles I and II:	3.7 hr.

Table XIII. Conventional Company Procedure for Dyeing Pantyhose

		Time (min.)
I.	Dyeing Batch I	
1.	Load machine	3
2.	Inject live steam 10 min. at 200°F	12
3.	Fill with cold water, and raise to 90°F	7
4.	Add auxiliary chemicals, run 10 min.	10
5.	Add dyes	1
6.	Raise temperature at 3°F/min. to 170°F	45
7.	Run 20 min. at 170°F	20
8.	Sample; make adds if necessary	10
9.	Dump the bath to drain when correct shade is obtained	3
II.	Finishing Batch I	
10.	Refill with cold water, rinse 10 min. and dump the bath	20
11.	Refill with cold water	3
12.	Inject steam rapidly to achieve 110°F	4
13.	Add finish chemical and run 10 min. at 110°F	10
14.	Dump the bath to drain	3
15.	Unload the pantyhose	3
	Cycle I Total:	154 min.
III.	Dyeing and Finishing Batch II	
1.	Repeat steps 1 through 15	
	Cycle II Total:	154 min.
	Total Time, Cycles I and II:	308 min. 5.1 hr.

quent batch. The mild prescour was placed in the reuse procedure in order to eliminate gross quantities of spin oils, oligomers, and other detrimental chemicals inherent in the fiber that could interfere with the dyeing behavior before reaching a level concentration in long-run sequences. No additional water, energy or chemical costs were incurred by incorporation of the prescour as it was utilized as obtained from the finish cycle. The scour chemical was placed in the dyebath at a 2% owf concentration in the conventional procedure. In the modified procedure, the scour chemical was added at a 1% owf concentration to the dyebath and at a 1% owf concentration in the separate scour bath, avoiding any overall chemical increase. The required dyebath analysis time (approximately 15-30 minutes) was concurrent with the 36 minutes necessary to finish Batch I and to prescour Batch II.

In discussing the future in-plant demonstration, the company expressed doubt that sufficient quantities of Nylon 66 pantyhose ncessary to conduct the demonstration would be required by company customers in the season in which the demonstration was planned. In addition, Nylon 6-based pantyhose had overtaken Nylon 66-based pantyhose as the company's largest volume style.

An additional thirteen-cycle reuse sequence on the pilot-scale machine was thus conducted which incorporated both Nylon 6 and Nylon 66 pantyhose in a range of five shades utilizing the procedure detailed in Table XII. The Nylon 66 batches were dyed by the three shades utilized previously in the ten-cycle reuse sequence (Table XI), and the Nylon 6 batches were dyed by two different shades incorporating the same three disperse dyes used to obtain the Nylon 66 shades.

The sequence is detailed in Table XIV. No unexplained problems were encountered during the sequence. The hosiery quality was judged acceptable and was later sold by the plant as first quality. Quantitative color difference calculations using the Diano LSCE Automate System and the FMC II Color Difference Metric Program confirmed that the hosiery fell below the three to seven MacAdam unit tolerance range that had been deciphered for the company (Table XIV). The sequence thus confirmed that on a pilot-scale basis the modified procedure was practical.

Savings and Cost/Benefit Analysis. The measured chemical and water savings for the initial 10- run reuse sequence over conventional procedures are contained in Table XV, along with the calculated energy savings based on a 200°F drop of the bath. The dye cost savings were low, due to the high exhaustion (90-97%) of disperse dyes attained with nylon. The cost savings on the auxiliary chemicals (leveling agents,scouring agents, penetrants, etc.) were impressive due to the lack of exhaustion and repeated batch-to-batch use of these materials. No process water had to be added for dyeing after the initial Run I fill. A 2% volume increase during each cycle caused by steam condensation offset minor fiber retentive losses, and thus water cost and subsequent sewer cost savings were also substantial.

Table XIV. Lot-to-Lot Color Differences in MacAdam Units of Nylon 66 and Nylon 6 Pantyhose Dyed with Disperse Dyes

Run Number	Fiber Type	Shade[a]	Color Difference Versus Standard
1	66	Light	1.96
2	66	Medium I	4.21
3	6	Medium II	2.87
4	6	Dark II	1.93
5	66	Dark I	2.79
6	66	Light	1.95
7	66	Medium I	2.98
8	6	Medium II	2.16
9	6	Dark II	2.41
10	66	Dark I	2.36
11	66	Light	2.99
12	6	Medium II	3.37
13	66	Light	4.21

[a] A total of five shades were utilized. The numeral I refers to a Nylon 66 shade, and the numeral II refers to a Nylon 6 shade.

Table XV. Chemical, Water, and Energy Savings in Application of Dyebath Reuse to Disperse Dyeing of Nylon 66 Pantyhose*

Chemical			
Dyes (%)	Auxiliaries (%)	Water (%)	Energy (%)
5.2	86	90	35

* Based on a 10-cycle dyeing sequence with a 200°F drop of bath

Using the savings figures from Table XV, a model pantyhose finishing plant incorporating dyebath reuse was constructed with the following assumptions:

1) The mill contained 16 rotating drum machines, all of 200-pound capacity, and 50% of the mill's production (Nylon 66) was adaptable to dyebath reuse. Eight of the machines would thus be equipped for reuse.
2) The plant used three eight-hour shifts per day, 50 weeks per year, and currently is able to complete three batch runs per machine per shift. The yearly production would thus be 7.2×10^6 lb/yr. with the production adaptable to reuse being 3.6×10^6 lb/yr.
3) The plant must purchase all of the tank/plumbing assemblies and necessary analytical tools in order to adapt the process to reuse. Two machines were operable from one holding tank by proper scheduling, and therefore four tanks were required.
4) The shade sequence of three light, three medium, and three dark was assumed to be followed by each 10 cycles of operation.
5) The rotary drum machine was assumed to be the basic unit, with no auxiliary components.
6) The maximum temperature reached during the cycle was assumed to be 200° C with no cooling cycle before pumping to the holding tank, and thus the energy savings detailed in Table X are considered to translate to the commerical process on a BTU/pound of dyed goods basis.

Using vender information and best estimates, Table **XVI** was compiled to estimate the capital investment required to convert the eight 200-pound rotary drum machines of the model hosiery plant to dyebath reuse, the tools required to attain the proper analytical capabilities, and the cost of operating supplies for one year. The assumption was made that two machines could be operated from one holding tank.

From Table XI, data from the participating company on the project, and measured data from the pilot-scale runs, Table XVII detailing the annual savings for the model plant was constructed. The water/sewer dollar savings was based on a combined cost of 50¢ /1,000 gallons, and the energy savings on $\$3/10^6$ BTU. Both figures are representative of 1978 cost figures for plants in the Southeastern United States. Combining the three savings factors, the described model plant would realize $73,700/yr. on reuse incorporation, or 2.05¢ /lb. of goods dyed during the year. Utilizing the data in Tables XVI and XVII, the return on the initial capital equipment costs for the model plant would be:

$$\frac{\$53{,}500 \text{ Capital Investment}}{\$73{,}700\ \frac{\text{Cost Savings}}{\text{Year}}} \times \frac{12 \text{ Months}}{\text{Year}} = 8.7 \text{ Months}$$

In Energy Conservation in Textile and Polymer Processing; Vigo, T., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 1979.

Table XVI. Estimate of Capital Equipment and Plant Supply Costs for Reuse Incorporation by the Model Pantyhose Operation

Modification or Analytical Tool	Basic Cost Per Unit ($)	Number Required (#)	Total Cost for 8 Machines ($)
Capital Equipment			
Chemical Add Tank	150	8	1,200
Insulated Stainless Tank	4,500	4	18,000
Pump and Plumbing System	4,000	4	16,000
Balance	1,100	1	1,100
Centrifuge	250	1	250
Spectrophotometer	3,500	2	7,000
Desk Computer	5,000	2	10,000
		TOTAL:	$53,500
Operating Supplies Inherent to Reuse			
Misc. Analytical Supplies (filters, syringes, etc.)	4,000		4,000
OVERALL FIRST-YEAR COST (Includes Installation Costs):			$57,500

Table XVII. Estimated Annual Savings for the Model Hosiery Plant on Incorporation of Dyebath Reuse to 3.6×10^6 lb./yr. Production

Item	Savings Basis	Savings Per Year ($)
Dyes and Chemicals	1.08¢/lb.	39,000
Water/Sewer	1.94×10^7 gal./yr.	9,700
Energy	2.27×10^3 BTU/lb.	25,000
	Total:	$73,700

The 8.7 month period is well below the normal industrial requirement of a one-to-two year return ofcapital investment(10).

Pressure Batch Dyeing of Polyester Yarn Packages.

Pilot-Scale Investigation. Poundage of polyester dyed in pressure equipment with disperse dyes has grown dramatically due to environmental problems connected with atmospheric carrier dyeing of the fiber. Table XVIII, which represents a "best estimate" of the current status on polyester batch dyeing, reflects the large volume of the synthetic dyed in pressure systems (11).

Georgia Tech did not possess modern pressure fabric dyeing equipment at the initiation of the dyebath reuse research. Therefore, to determine the feasibility of dyebath reuse in the general area of coloration of 100% polyester under pressure with disperse dyes, research was initiated on available package yarn equipment.

The goal was to determine the feasibility of reusing the residual hot dyebath resulting form high pressure package dyeing of both spun and textured filament 100% polyester yarn. Both single shade and multishade dyeing series were initially conducted using disperse dyes on a single-package Morton pressure machine. Standard mill procedures and materials were utilized in conjunction with reuse. A summary of the dyeing series is shown in Table XIX, while color formulations are detailed in Table XX. Reuse of an auxiliary bath, a sodium hydroxide/sodium hydrosulfite reduction clearing bath that was utilized to clear unfixed dye from the polyester, was accomplished in conjunction with dyebath reuse in the final sequence. Analysis of the disperse dyebath was the general procedure detailed in the introduction to this chapter.

The experimental details and results for the dyeing Series I through VII (Table XIX) in which only dyebath reuse was utilized have been reported elsewhere (8). The dyed packages were quantitatively analyzed for both through-package as well as lot-to-lot shade variation. For example, Table XXI details the color differences between fabric samples knitted from yarn unwound at set positions from selected packages of Series II, Table XIX (8). In Series II, eight packages were dyed to the same green shade from a common bath. With a few exceptions, such as Position 1 of Package 2, the packages demonstrated good through-package uniformity. Exhaustion in the disperse pressure system was found to be so high (96-99%) that multishade sequences not in a color line could be dyed satisfactorily with reuse if at least one dye overlapped and if care was observed in choosing the shade sequence. Table XXII gives the through-package and average color differences of the multishade Series VI dyeings from Table XIX (8). With the exception of the maroon shade, the color differences were considered reasonable for the pilot-scale system.

Table XVIII. Estimated Polyester Dyed in Pressure Equipment, 1978 (10) (Millions of Pounds)

Fiber Form	End Use	Type Structure	Package	Beam	Pressure Jet	Pressure Beck
Filament	Apparel	Broadwoven	16	--	57	5
		Knit-circular	100	--	599	237
Staple	Apparel	Knit-circular	126	10	55	10
		Totals:	142	10	711	252

Grand Total, 1978: 1115 x 10^6 lb.

Table XIX. Summary of Pressure Package Dyeing Series Utilizing Reuse

Series	Shade	Number of Dyes	Yarn Type	Packages in Series
I	Pink 2	1	Spun	8
			Textured	3
II	Green	2	Textured	5
			Spun	3
III	Gray	3	Spun	5
			Textured	3
IV	Pink 1	1	Spun	1
	Blue	3	Spun	2
	Green	2	Spun	2
	Yellow	2	Spun	2
	Gray	3	Spun	2
VI	Pink 1	1	Textured	1
	Yellow	2	Textured	1
	Blue	3	Textured	1
	Green	2	Textured	1
	Gray	3	Textured	1
	Maroon	3	Textured	1
VII	Yellow	2	Spun	1
	Blue	3	Spun	1
	Maroon	2	Spun	1
	Yellow	2	Textured	1
	Blue	3	Textured	1
	Maroon	2	Textured	1
VIII	Blue	3	Textured	5
	Green	2	Textured	1
	Blue	3	Textured	1
	Gray	3	Textured	1
	Maroon	2	Spun	1

Table XX. Color Formulations

Light Shades:

- Pink I
  - 0.12% Disperse Red A
- Yellow
  - 0.53% Disperse Yellow
  - 0.06% Disperse Orange

Medium Shades:

- Pink II
  - 1.20% Disperse Red A
- Blue
  - 1.75% Disperse Blue A
  - 0.73% Disperse Blue B
  - 0.03% Disperse Yellow
- Green
  - 2.15% Disperse Blue A
  - 1.30% Disperse Yellow

Dark Shades:

- Gray
  - 1.10% Disperse Blue C
  - 0.65% Disperse Orange
  - 0.032% Disperse Red B
- Maroon
  - 3.70% Disperse Rubine
  - 0.16% Disperse Orange

Table XXI. Color Difference Values for Series II Dyeings of a Green Shade

Package Number	Yarn Type	Color Differences in MacAdam Units[a] (Position of Yarn in Package)					Average Color Difference Versus Standard
		1	2	3	4	5	
1	Textured	4.38	0.73	1.70	1.46	1.43	Standard
2	Textured	7.79	2.38	2.93	4.86	3.68	1.90
3	Textured	2.30	1.90	3.31	3.67	3.65	2.35
4	Textured	7.55	2.37	2.86	5.54	5.84	1.35
5	Textured	1.56	2.58	1.84	2.86	3.11	1.86
6	Spun	3.48	1.89	2.46	1.89	1.12	Standard
7	Spun	3.80	1.21	1.49	2.61	1.81	1.47
8	Spun	2.39	1.54	1.72	1.57	1.29	1.30

[a] Color differences between each fabric and its standard.

Subsequent research was directed toward reuse of both the dyebath and the sodium hydrosulfite/sodium hydroxide reduction clearing bath utilized by the participating plant. Both components were colorless, and thus simple quantitative analysis could not be performed. In analysis of the reduction clearing bath the sodium hydrosulfite, which was involved in a chemical reaction with the unfixed dye, was arbitrarily assumed to be depleted by 10%. The hydrosulfite was suspected of being present in huge excess, with destruction on reaction with the dye considered to be minimal. The 10% was added to the next bath while also accounting for differences in package weight and liquor loss. Sodium hydroxide addition to the original bath had resulted in a pH of approximately 11.7. Sufficient sodium hydroxide was thus added to each subsequent bath after hydrosulfite replenishment to maintain the initial pH of 11.7. A holding tank separate from the dyebath tank was required for the clearing bath.

The dyeing sequence which reused both the dyebath and the reduction/clearing bath was Series VII of Table XIX. Color difference values between the dyed packages and standards are detailed in Table XXIII. Run 7 produced a blue which dyed heavily on the outside and very lightly throughout the rest of the package, as evidenced by the lack of through-package uniformity. The poor dye penetration was attributed to a machine malfunction affecting the in-out pressure flows. The gray shade of Run 8 was also considerably out of reasonable commercial limits, dyeing darker than previously experienced; the system corrected itself, however, on Run 9.

To further determine the effect of reusing the reduction/clearing bath on the dyed yarn properties, lightfastness and crockfastness tests were performed on standard-dyed fabrics, dyebath reuse-dyed fabrics, and dyebath reuse plus reduction bath reuse-dyed fabrics. Lightfastness was performed according to AATCC Test Method 16A-1974, which called for forty hours of exposure to a carbon arc. Crockfastness was performed according to AATCC Test Method 8-1972. All fabrics exhibited the same fastness properties, indicating that the semiquantitative replenishment of the caustic/hydrosulfite bath did not affect the yarn quality.

Savings and Cost/benefit Analysis. Energy usage was calculated for a conventional mill dyeing series and a dyebath reuse series conducted on the Morton Laboratory Machine. The conditions of times and temperatures were based on Series V of Table XIX. Water usage was calculated for both conventional and reuse dyeings based on the laboratory machine volumes and on Series V dyeings. Chemical and dye savings were also calculated for Series V for the laboratory scale procedures. The values were compared with the amounts of dyes, chemicals and water which would have been necessary if conventional procedures had been utilized. Water, chemical and energy savings associated with reduction bath reuse were also compiled. A summary of the

Table XXII. Color Difference Values for Series VI Dyeings on Textured Yarn

Package Number	Shade	Color Differences in MacAdam Units (Position of Yarn in Package) 1	2	3	4	5	Average Color Difference Versus Standard
1	Pink	5.47	1.40	1.02	2.09	1.33	Standard
2	Yellow	1.94	2.96	3.65	5.23	3.76	2.79
3	Blue	3.65	2.05	3.12	4.25	5.40	1.78
4	Green	2.64	3.20	3.16	3.21	2.30	2.84
5	Gray	3.66	5.02	4.33	5.44	4.10	4.33
6	Maroon	9.01	8.51	8.49	8.00	9.07	8.47

Table XXIII. Color Difference Values for Series VII Dyeings on Textured Yarn Incorporating Both Dyebath Reuse and Reduction Bath Reuse

Package Number	Shade	Color Differences in MacAdam Units (Position of Yarn in Package) 1	2	3	4	5	Average Color Difference
1	Blue	3.21	2.31	1.84	1.30	1.41	1.87
2	Blue	4.12	3.06	1.74	1.37	1.17	1.77
3	Blue	7.38	5.05	4.43	3.73	4.11	4.90
4	Blue	4.17	2.37	1.02	1.57	0.65	1.35
5	Blue	1.48	1.40	1.31	0.65	1.99	1.30
6	Green	2.82	3.23	2.97	2.68	3.29	2.82
7	Blue	10.40	4.47	5.39	6.52	8.53	4.21
8	Gray	6.40	9.71	12.56	13.59	14.33	11.14
9	Maroon[a]	5.29	5.61	4.94	4.41	4.50	4.68

[a] Spun yarn utilized only for this run.

Table XXIV. Chemical, Water, and Energy Savings in Application of Dyebath/Auxiliary Bath Reuse to Package Dyeing

Procedure Used	Dye Cost (%)	Auxiliary Cost (%)	Water (%)	Temp.	Energy (%)
Dyebath Reuse	2.2	82.0	81.0	250°F	56.1
				272°F	50.3
Reduction Bath Reuse	---	76.2	89.0		74.0
Dyebath and Reduction Bath Reuse	2.2	77.8	85.0	250°F	63.5
				272°F	59.4

results is shown in Table XXIV, with the combined system tabulated in Row 3 of the table.

A model package dyeing plant constructed for the cost/benefit analysis of applying dyebath/auxiliary bath reuse to pressure package dyeing was assumed to have the following:

1) The energy consumption per lb. of goods for the conventional procedure was assumed to be the same as that determined for the participating plant on the project using data supplied by the plant personnel, 5.05 x 10^3 BTU/lb. The figure includes the steps through the reduction/clearing cycle and the subsequent rinses, but does not include any finishing operations which were the same for conventional and reuse-dyed yarn. The plant operated a heat exchanger, and the recovered heat was included in all the energy calculations.
2) For a ten-cycle dyebath reuse sequence, the average energy consumption was calculated, using plant data and Table XXIV, to be 2.85 x 10^3 BTU/lb. Ten cycles was conservatively assumed to be the maximum number of cycles that the model plant could adequately schedule.
3) The model plant was assumed to contain five package dyeing systems operating at a 10:1 liquor ratio. Each system consisted of two pressurized machines, each capable of holding 1,000 pounds of yarn. The machines were tied in tandom by a pumping system so that large lots (2,000 pounds total) of a single shade could be dyed from the same circulating liquor. Production to which reuse could be applied was assumed to be 60% of the total, and thus three of the dyeing systems, incorporating six machines, had to be equippped for reuse. Three holding tank/plumbing systems were thus assumed for the operation, allowing one holding tank per dyeing system.
4) The plant was assumed to complete three batches per shift on each of its dyeing systems, and to operate three shifts per day, five days per week on a 50-week work year. Thus on the three systems to be converted to reuse, a year's production totaled 1.35 x 10^7 lb./yr.
5) No increase in production was assumed as a result of reuse incorporation. Also, 10 cycles per reuse sequence was conservatively assumed to be the maximum number of batches dyed from the same bath in the plant setting.

Incorporating vendor data, Table XXV details the capital equipment needed to convert the three dyeing systems to dyebath/reduction clearing bath reuse, and the cost factors for the components. The table also contains the estimate for the software costs per year, and the total first-year costs.

Table XXVI summarizes the annual combined cost savings per year for the model plant on reuse adaptation, a total of \$305,600/year (2.3¢/lb). The savings were based on the Table XXIV data, participating plant data, and cost factors of \$3/10^6 BTU for energy and 50¢/1,000 gal for water/sewer costs. Utilizing

Table XXV. Capital Equipment and Operating Cost Estimate for Dyebath Reuse Applied to Polyester Package Dyeing

Capital Equipment	Cost[a] ($)
Holding Tank, 2,500 gal., 6, @ $10,000 each	$ 60,000
Pump/Plumbing Systems, 6,@ $5,000 each	30,000
Balance, 1	1,500
Centrifuge, 1	250
Spectrophotometer, 1	3,000
pH Meter with electrodes, 1	1,000
Desk Computer with printout, 1	4,500
Total:	$100,250
Operating Supplies Per Year	
Filters, Syringes, etc.	$ 4,000
Total First-Year Cost:	$104,250

[a] Includes installation costs.

Table XXVI. Combined Cost Savings in Adaptation of Dyebath Reuse to Polyester Package Dyeing at 1.35 x 10^7 lb./yr. Production

Item	Savings Basis	Cost Savings ($/Year)
Energy	2.2 x 10^3 BTU/lb.	89,100
Dyes and Chemicals	1.52¢/lb.	205,000
Water/Sewer	2.15 gal./lb.	14,500
	Total:	$308,600

the data in Tables XXV and XXVI, the recovery of capital investment would be accomplished in:

$$\frac{\$100{,}250 \text{ Capital Investment}}{\$308{,}600 \text{ Cost Savings/Year}} \times \frac{12 \text{ Months}}{\text{Year}} = 4 \text{ Months}$$

Including the $4,000 operating costs, the model plant would thus realize $204,350 profit the first year, and $308,600 each year thereafter, neglecting tax incentives and maintenance/repair costs on the added equipment.

Reactive Dyeing of Cotton and Cotton/Polyester Blends.

Pilot-scale Investigation. Approximately 1.3 billion pounds of the textile fabrics and yarns that are annually batch-dyed are composed of 100% cotton or some percentage of cotton/polyester blends (2). The three major dye classes that have been utilized in recent years to color cotton-containing fabrics are vats, directs and reactives for 100% cotton, and these dyes plus disperse dyes for cotton/polyester blends. Several recent events,however, have limited the choices of dye classes available to dyers. Several chemical manufacturers have terminated the production and sale of vat dyes dyes to cost factors and mercury pollution inherent in the process. In addition, several high-volume direct dyes have recently been found to cause cancerous livers in rats (9). Speculation was that the tested disazo direct dyes (Direct Blue 6, Direct Black 38, and the copper complex of Direct Brown 95) may be metabolized in the body to the precursor benzidine, which is one of the most potent carcinogens known. The possibility exists, therefore, that the U.S. production of vat and disazo direct dyes will be curtailed in the foreseeable future.

Due to the potential regression in supply and use of disazo directs and vats as well as more strenuous wet fastness requirements, textile firms dyeing cotton-containing fabrics are projected to switch production to reactive dyes in increasing numbers. Reactive dyes are unique in that the dye with the cellulose in cotton or rayon. In the process the material is impregnated with the reactive dye, base is added to the bath to effect the dye/fiber chemical reaction, and the fabric is then carried through an afterscour. Reactive dyes have several severe drawbacks:

1) The dyes are among the most expensive marketed, typically costing $5-20/lb.
2) The dyes exhibit poor exhaustion on the fiber, leaving 20-40% of dye in the bath.
3) Large quantities of unexhausted auxiliary chemicals, such as salt and base, are wasted in the process.
4) A large portion of the reactive dye is hydrolzyed by the base before fixation, resulting in "inactive" hydrolyzed dye that is difficult to remove from the fabric and necessitating high-energy afterscour operations.

5) Reactive dyes will not color polyester, and thus the conventional process for dyeing blends consists of four distinct and separate procedures: dyeing of the polyester with disperse dyes, reduction/clearing of the polyester, impregnation of the cotton component with reactive dyes, and fixation of the reactive dye.

The latter disadvantage is especially severe from an energy viewpoint (10). Such four-cycle sequences in which no baths are reused are time-consuming (as long as twelve hours for beck fabric dyeing) and extremely energy-inefficient (16,000 to 26,000 BTU/lb. of goods) (11).

In summary, considerable costs are associated with direct energy consumption and waste in conventional reactive dyeing of cotton-containing textiles as well as chemical losses, water waste, increased pollution loads, and lost production time. In addition, indirect energy losses inherent in chemical production, water purification, pollution treatment, and plant operation must be considered for reactive dyeing due to the low dye exhaust, high auxiliary use, and increased water requirements that are far removed from other dye classes. With the potential of dyebath reuse demonstrated in other areas of batch dyeing, adaptation of dyebath/auxiliary bath reuse to reactive dyeing of cotton-containing textiles was imperative.

The initial reuse research dealt with dyeing of 100% cotton knit underwear fabrics. The approach was to dye 100% cotton with a single reactive dye (low-temperature) in order to determine the initial problems in adapting reuse to reactive dye systems. The analysis of the reactive dyebath was similar to that described for disperse dyes in the general discussion section of this chapter. Since the reactive dye was water soluble, no organic extraction was necessary before analysis. The problems encountered and the solutions derived in this stage were:

1) Prevention of dye hydrolysis--Hydrolyzed reactive dyes, in which the reactive group has been replaced by an inactive group, are colored (12). Due to the spectrophotometric interference of this colored impurity, the prevention of dye hydrolysis (always present in conventional systems when base is added) was an important priority. A "split-bath" technique, modeled after continuous dyeing operations, was devised so that the reactive dye impregnation bath was never contacted with base. This approach necessitated two holding tanks, but allowed for reuse of both baths without effecting the analysis scheme. A flow diagram for the 100% cotton system is shown in Figure 1.
2) Step-up in exhaustion--When base is added to the dyebath in conventional reactive dye systems, a "step-up" in exhaustion occurs due to the shift in dye equilibrium caused by fixation to the fiber (13). In the split-bath system, where the fixation bath is introduced, such a step-up is impossible. As a result, a higher concentration of dye then called for by the conventional procedure was necessary in

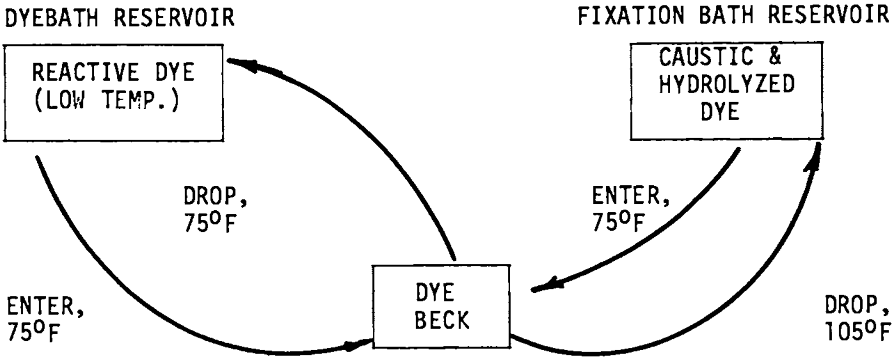

Figure 1. Dyebath reuse 100% cotton/low-temperature reactive dyes

Table XXVII. Dyebath Reuse Color Difference Calculations: 100% Cotton/One Low-Temperature Reactive Dye

Sample	Color Difference (MacAdam Units)
1	Standard
2	1.5
3	2.3
4	2.9
5	1.8

the impregnation bath in order to exhaust the same mass of dye on the fiber, and thus match shades in the two systems.

Prediction of the excess dye necessary to reach the upper exhaust level required development of a computer program. In the initial studies, however, a "best estimate" was made as to the proper excess. Good lot-to-lot shade matching was obtained, as shown in the low color differences exhibited in Table XXVII. Color differences with a conventionally-dyed sample were high, however, due to the inaccuracy of the "best estimate" method in determining the dye excess.

3) Bleed-off of dye in fixation bath--When the fixation bath was pumped into the container with the impregnated fabric, dye back-off occurred, resulting in lighter shades. Addition of copious salt to the fixation bath did not completely eliminate the problem. Therefore, when the fixation liquor was initially made up, reactive dye in equivalent concentration to the dyebath was added and hydrolyzed. The hydrolyzed dye in the fixation bath effectively prevented back-off of the unhydrolyzed dye on the fabric.

4) Long-term dye stability--Low-temperature reactive dyes will slowly hydrolyze with water over long periods of time, even at room temperature. To prevent slow hydrolysis, the dye impregnation bath was kept at a slightly acid pH (~ 6.0). This technique proved successful, with dye solutions maintained for several weeks without detectable degradation.

After the initial problems were solved, samples of 100% cotton knit fabric were dyed on a beaker scale five times from the same single-dye impregnation and fixation bath. The color differences between the fabrics and the initial dyeing (chosen as the standard) were within the desire two to four MacAdam unit range (Table XXVII).

In the next series of experiments, a procedure incorporating three low-temperature reactive dyes was attempted on 100% cotton. The procedure was modeled after a participating company's formulation. The flow system detailed in Figure 1 was utilized, and the methods developed for the one-dye system were used to attempt shade match with the company standard. Additional problems that arose with the three-dye system were as follows:

1) Dye blends--One of the reactive dyes, a scarlet, was a blend, composed of an orange component and a red component. The orange and red components exhausted at different percentages, thus blocking analysis and dye blend adds. The dye manufacturer provided Georgia Tech on a confidential basis with a detailed analysis of the dye blend, allowing reuse analysis and adds of the individual components.

2) Overlapping spectrophotometric curves--The multidye system contained dyes whose spectrophotometric curves overlapped, hindering simple analysis. A 16-point computer program, in

which absorbance values at 16 wavelengths across the visible region were taken instead of only peak values, was thus developed for accurate analysis of the exhausted baths (see introductory section).

A total of six cotton knit fabrics were then dyed using the multidye procedure and utilizing the split bath reuse technique. The color differences between the average of all the reflectance measurements obtained for the six samples and the individual fabrics ranges from 0.3-1.5 units, and the differences between the first sample and the following five ranged from 1.0-3.1 MacAdam units (Table XXVIII). All the color differences were well within acceptable lot-to-lot tolerance ranges. However, due to the "best estimate" method used to determine the excess dye required to match the correct exhaustion level, a poor shade correlation with the company standard was obtained. A computer program designed to accurately predict the required excess dye and being developed at Georgia Tech will allow closer shade matches with the standard.

The final area of knit fabric research was adaptation of reuse to the coloration of 50/50 cotton/polyester blends. Several problems in addition to those already listed had to be attacked and solved before the process could be developed:

1) Reduction of cycles--As detailed earlier, four distinct and separate procedures are required to dye cotton/polyester blends in conventional processes: disperse polyester dyeing, reduction/clearing reactive impregnation of the cotton component, and reactive dye fixation. To reduce the number of steps, a high-energy reactive dye and what was initially through to be a base-stable disperse dye were used. The flow diagram for the process is detailed in Figure 2. By using the high-temperature reactives, polyester disperse dyeing/cotton reactive impregnation were accomplished from the same bath. The 170° F caustic fixation bath provided reduction clearing for the disperse dye while simultaneously effecting chemical fixation.
2) Dyebath analysis--To analyze the combined dyebath containing the relatively water-insoluble disperse dye and soluble reactive dye, benzene extraction was utilized to separate the two classes. The disperse dye, extracted into the benzene layer, was readily analyzed, as was the reactive dye remaining in the water layer.

The number of distinct cycles neecessary to dye the blend fabric was thus reduced from four to two. Using reuse in conjunction with the shortened process, six fabrics were dyed and analyzed. The color differences between the average of all the reflectance measurements and the dyed fabrics ranged from 2.5-5.7 MacAdam units, while those between the first dyed sample and the remaining five fabrics ranged from 3.6-8.5 MacAdam units (Table XXIX), all within or slightly outside the desired lot-to-lot shade tolerances. The color difference with a conventionally-

Table XXVIII. Dyebath Reuse Color Difference Calculations: 100% Cotton/Three Low-Temperature Reactive Dyes

Sample	Color Difference Versus Average	Color Difference Versus #1	Color Difference Versus Company Standard
1	1.6	Standard	14.6
2	1.1	1.0	14.7
3	0.7	1.4	14.8
4	1.1	2.5	15.4
5	0.3	1.8	15.3
6	1.3	3.1	15.4

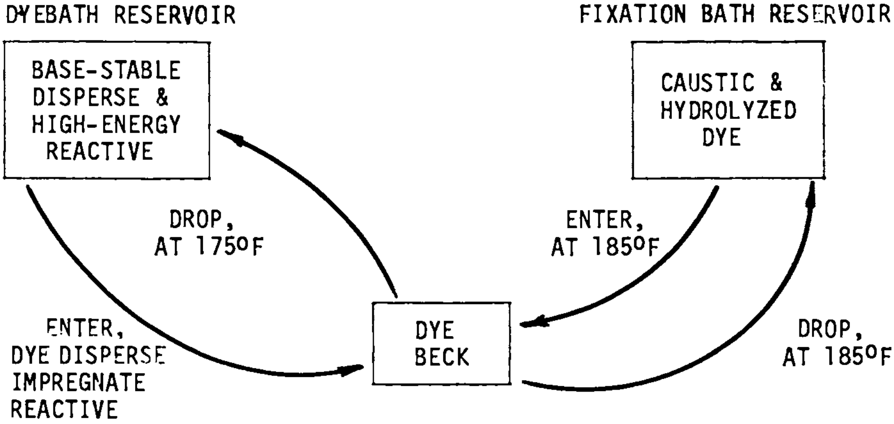

Figure 2. Dyebath reuse 50/50 cotton/polyester, high energy reactive/base-stable disperse

dyed sample, however, was extreme (80.2 MacAdam units). The "best estimate" procedure for determining the reactive dye excess, as well as a purplish shading that resulted when the fabric was contacted with the base fixation bath at 170°C, precipitated the large color difference.

Conversation with the dye manufacturer revealed a mistake had been made in recommendation of the disperse dye to be used in conjunction with the high-energy reactive dye. The recommended dye was an azo-based dye that was not stable to base at high temperatures, and degradation caused the purplish shade shift observed in the research. For future investigations, an anthraquinone-based disperse dye that is base-stable at 170°C has been recommended by the manufacturer for use with the high-energy reactive dye.

Savings and Cost/Benefit Analysis. The bench scale experiments were successful in overcoming major technical problems while demonstrating that dyebath/auxiliary bath reuse is indeed feasible with reactive dyes on cotton-containing fabrics. In addition, a shortened-cycle dyeing procedure coupled with reuse for cotton/polyester blends was shown to further increase energy, mass, and time savings (Table XXX).

To construct a model plant for incorporation of the two-step dyebath/fixation bath reuse technique to the coloration of cotton/ polyester knits, several assumptions were made:

1) The model plant was assumed to consist of 12 becks, each capable of processing 800 lbs/load at a liquor ratio of 14:1 (1350 gallons of water/load). of the production capacity, 50% was presumed applicable to two-step dyebath reuse, and therefore six production becks were outfitted for reuse.
2) Two becks were assumed to be operable from each holding tank, and thus six holding tanks for both dyebaths and fixation baths and six pump/plumbing systems were required.
3) Conservatively, no time savings were assumed in incorporation of the two-step dyebath/fixation bath technology, even though the reduced number of process steps over the four-step conventional procedure dictated increased productivity.
4) For the two-step reuse system, the same auxiliaries as utilized in the conventional process system were assumed, and the reactives and disperse dyes of the conventional process were assumed to be replaced on a one-to-one basis by high-energy reactive dyes and base-stable disperse dyes in the reuse procedure.
5) To simplify the calculations, the shade was considered constant for the ten cycles (a bright, heavy red). Exhaustion was considered to be a uniform 60% for the high-energy reactive and 90% for the disperse dyes.

Table XXIX. Dyebath Reuse Color Difference Calculations: One High-Energy Reactive Dye/One Disperse Dye

Sample	Color Difference Versus Average	Color Difference Versus #1	Color Difference Versus Company Standard
1	5.7	Standard	80.2
2	3.9	4.5	--
3	2.5	3.6	--
4	3.6	7.0	--
5	4.9	8.5	--
6	5.1	7.6	--

Table XXX. Energy and Water Savings in Adapting Dyebath/Fixation Bath Reuse to Combined Disperse/Reactive Dyeing of Polyester/Cotton Knit Fabric

Process	Energy Consumption Per Pound (BTU/#)	Energy Savings (%)	Water Consumption (Gal./#)	Water Savings (%)
Conventional	18,340	--	37.2	--
Reuse	11,968	35	20.6	45

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ACS Symposium Series; American Chemical Society: Washington, DC, 1979.

6) In regeneration of the fixation bath, no dye was added for hydrolysis after the initial cycle as in the pilot-scale research. The pH, based on laboratory trials, generally remained around 10.5-11.0, and therefore only a 10% addition of soda ash to the fixation bath for each reuse cycle was assumed. No salt or sequesterant was added after the initial fixation cycle.
7) For the auxiliary chemicals in the dye impregnation bath, carrier was considered to be totally exhausted, and thus was added at a 100% rate each cycle.
8) The annual production, based on an 800 lb/batch load, was calculated as follows:

$$\frac{8.00 \times 10^2 \text{ lb.}}{\text{Machine-cycle}} \times 6 \text{ Machines} \times \frac{1 \text{ Cycle}}{\text{Shift}} \times \frac{3 \text{ Shifts}}{\text{Work-day}} \times$$

$$\frac{5 \text{ Work-days}}{\text{Work-week}} \times \frac{50 \text{ Work-weeks}}{\text{Year}} = 3.6 \times 10^6 \text{ Pounds/Year Production}$$

The capital equipment required to outfit the model plant is located in Table XXXI, along with the relevant costs. The estimated annual cost for operating supplies and equipment as well as the total first-year cost are also included in the table.

The calculated annual cost savings for the model plant are contained in Table XXXII, and totaled $185,500/yr. (5.2¢/lb.) The savings were based on Table XXX, measured pilot-scale data, and data from the participating plant. The energy calculations included energy recovered from the plant's heat exchanger, and a cost factor of $\$3/10^6$ BTU was utilized to determine the annual cost savings. A water/sewer cost factor of 50¢ /1,000 gal was also utilized. The recovery of the capital investment, assuming no tax benefits, would be accomplished in:

$$\frac{\$108{,}350 \text{ Capital Costs}}{\$185{,}500 \text{ Annual Savings}} \times 12 \text{ Months} = 7 \text{ Months}$$

The model plant would thus realize $73,150 of profit the first year in incorporating the new technology. In the second and subsequent years, neglecting any maintenance and repair costs on the added equipment, the company would realize $181,500/yr. profit.

Indirect Energy Savings

The energy savings in the cost/benefit calculations were direct energy savings for the model textile finishing plants. From a national viewpoint, dyebath reuse also offers considerable indirect energy savings. Although data on the energy required to produce each dye and chemical utilized in the process, to purify

Table XXXI. Estimate of Capital Equipment Costs and Annual Operating Costs on Reactive/Disperse Reuse Incorporation

Capital Equipment		Cost ($)
Holding Tank, 6, @ $11,500 each		$ 68,000
Pump/Plumbing System, 6, @ $5,000 each		30,000
Water Meter, 3,@ $300 each		900
Chemical Add Tank, 3,@ $200 each		600
Balance, 1, @ $1,100 each		1,100
Centrifuge, 1, @ $250 each		250
Spectrophotometer, 1, @ $3,000 each		3,000
Desk Computer with printout, 1, @ $4,500 each		4,500
	Total:	$108,350
Annual Operating Supplies		
Filters, Syringes, Glassware, etc.		$ 4,000
	Total First-Year Cost:	$112,350

Table XXXII. Direct Savings in Two-Step Dyebath Reuse Coloration of Cotton/Polyester Knits Based on 3.6 x 10^6 Lb./Yr. Production

Item	Savings Basis	Annual Cost Savings ($)
Energy	6.3 x 10^3 BTU/lb.	$ 68,800
Dyes and Chemicals	2.41¢/lb.	86,800
Water/sewer	16.6 Gal./lb.	29,900
	Total:	$185,500

a gallon of water, or to effectively treat a gallon of sewer waste was unavailable to the authors, some conclusions can be drawn from the derived percentage decreases. For example, since cost is directly proportional to weight, the weight of chemical savings defined for the ten-cycle reuse sequence on pantyhose would be 26% (Table XV). Since the energy to produce the chemicals is directly related to the weight on a BTU/lb basis, that necessary to manufacture the chemicals required to dye 10 batches of pantyhose by reuse would also be reduced by 26%.

The marked reduction in required water exhibited by the reuse processes would amount to substantial savings in treatment chemicals such as chlorine (and the corresponding energy required to produce them), and in the electricity required to pump and filter the process water. Energy required to treat sewer streams, such as electrical power to operate pumps for aeration, would also be reduced proportionately to the volume decrease. In relation to the 1985 zero discharge standards recently published by the EPA, sewage treatment costs are expected to rise significantly in the next decade, thus accentuating the importance of incorporating dyebath reuse.

Summary

Dyebath/auxiliary bath reuse has been demonstrated on a pilot-scale to be a feasible, economical alternative to conventional batch dyeing processes. Atmospheric disperse dyeing of nylon and polyester carpet and nylon pantyhose, and pressure disperse dyeing of polyester yarn packages have all been demonstrated as suitable candidates for plant incorporation of the reuse techniques.

Good lot-to-lot shade correlations were also obtained with reuse of low-temperature reactive dyebaths and fixation baths on 100% cotton, and with reuse of combined high-energy reactive/disperse dyebaths and fixation baths on cotton/polyester knit fabrics. Further computer program development is required, however, before industrial shades can be matched with the reactive dye reuse system.

Substantial savings in energy, dye, chemical, and water/sewer requirements have been demonstrated, and cost/benefit analyses based on the pilot-scale data and industrial information indicate a recovery of capital investment of less than one year for all of the systems investigated on incorporation of dyebath/axuiliary bath reuse.

An in-plant demonstration of dyebath reuse applied to coloration of nylon pantyhose has recently been completed, and the results will be published elsewhere (14).

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Literature Cited

1. Anonymous, "In-Plant Control of Pollution: Upgrading Textile Operations to Reduce Pollution", Technology Transfer Seminar Publication EPA-62513-74-004, Environmental Protection Agency, Washington, D.C. 1974.

2. Lowry, J.F., Cook, F.L., et al., "Energy Conservation in the Textile Industry", Phase I Technical Report of Department of Energy Project No. EY-76-S-05-5999, Engineering Experiment Station and School of Textile Engineering, Georgia Institute of Technology, Atlanta, Georgia, 1977, p. 36.

3. Lowry, J.F., Cook, F.L., et al., Ibid, p. 29.

4. Giles, C., "Notes for a Laboratory Course in Dyeing", Society of Dyers and Colorists, Yorkshire, England, 1966, p. 53.

5. Judd, D.B. and Wyszecki, G., "Color in Business, Science, and Industry", 3rd Ed., John Wiley and Sons, New York, N.Y., 1957, p. 322.

6. Tincher, W.C., "Conservation of Water, Chemicals and Energy in Dyeing Nylon Carpet", Final Technical Report ERG-07-77 of Office of Water Research and Technology Project No. A-064-GA, School of Textile Engineering, Georgia Institute of Technology, Atlanta, Georgia, 1977.

7. Tincher, W.C., Am. Dyest. Rep., (1977), 66(5), 36.

8. Cook, F.L. and Tincher, W.C., Text. Chem. Color., (1978), 10(1), 1.

9. Anonymous, "Direct Blue 6, Direct Black 38, and Direct Brown 95: Benzidine Derived Dyes", Current Intelligence Bulletin No. 24, U.S. Department of Health, Education and Welfare, Washington, D.C., 1978.

10. Lowry, J.F., Cook, F.L., et al., "A Study of Barriers to Energy Conservation Technology in the Textile Industry", Technical Report of Argonne National Laboratory Contract No. 31-109-38-4056L, Engineering Experiment Station and School of Textile Engineering, Georgia Institute of Technology, Atlanta, Georgia, 1977.

11. Cook, F.L., Carr, W.W., et al., "Energy Conservation in the Textile Industry", Phase II Technical Report of Department of Energy Project No. EY-76-S-05-5099, Engineering Experiment Station and School of Textile Engineering, Georgia Institute of Technology, Atlanta, Georgia, 1978.

12. Trotman, E.R., "Dyeing and Chemical Technology of Textile Fibers", 5th Ed., Chapter 22, Charles Griffin and Company, Ltd., London, England, 1975.

13. Dolby, P.J., Book of Papers 1977 AATCC National Technical Conference, Atlanta, GA., Oct. 19-21, 1977, p. 179.

14. Cook, F.L., Tincher, W.C., et al., "In-Plant Demonstration of Dyebath Reuse Applied to Hosiery Dyeing", Phase III/ Part I Technical Report of Department of Energy Project No. EY-76-S-05-5099, Engineering Experiment Station and School of Textile Engineering, Georgia Institute of Technology, Atlanta, Georgia, 1979.

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17

Energy Consumption and Conservation: Textile Drying

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Half of the total energy consumption involved in the manufacture of finished textile fabrics is attributed to drying. Moreover, the textile industry in the United States is among the top ten industrial users of energy. Accordingly, it is imperative that the phenomena concerning the drying of fabrics during manufacturing are well understood and documented so that all efforts to minimize energy usage yet maintain production are exercised.

This paper presents a comprehensive study concerning energy usage during the drying of fibrous materials. Most of the research concerning drying has been coordinated by the paper industry; consequently, it is necessary to draw from that research to further the understanding of textile drying. Although there have been some outstanding contributions by researchers in the textile industry [Beard and Beckwith (1), Hebrank and Brown (2), and Lyons and Vollers (3)], it would not be unfair to emphasize the need for further and broader intensive study.

Within the context of this work drying by mechanical and thermal methods are investigated. The economics and effectiveness of systematically combining the two methods are also considered.

MECHANICAL DEWATERING

Water is either chemically or mechanically bound to textile fabrics. Most forms of chemical bonding occur by hydrogen bonding between a cellulose fiber (i.e., cotton or rayon) and the water molecule. The latent heat of vaporization is necessary to break the bond. Mechanical extraction techniques are generally not suitable for releasing the water molecule from the fibrous substrate. Water which is not chemically bound to the textile material is readily amenable to mechanical dewatering techniques. Major obstacles to the limit of mechanical dewatering besides hydrogen bonding are the surface tension between the water and the fiber and the ratio of fiber surface area to water content.

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The former property suggests that a lower surface tension will result in a lower limit of moisture removal while the latter property (a function directly proportional to fiber denier) will prevent significiant extractions provided the ratio is high. Further discussion of these obstacles is presented in a paper by Kuppers(4). Mechanical extraction may be performed by several well known or newer methods. The most common extraction device is the simple pad or squeeze roller. Moisture content after padding is about 75% for a 65% polyester/35% cotton poplin fabric. The energy required for padding is that which drives the motor and turns the mangle. A typical mangle might require a 5 horsepower motor. Assuming that the entering fabric is soaking wet or at about 150% moisture content and exits at 75% moisture content, the energy required per kg of water removed is 50,000 Joules/kg of water. This calculation considers the inherent electrical generation efficiency and represents the thermal energy required per kilogram of water removed. While squeezing techniques are very energy efficient they are not always applicable. For instance, high pile fabrics and tufted structures can be virtually destroyed if processed through squeeze pressures required for dewatering.

Another efficient mechanical extraction technique uses an ambient air temperature suction process. In the textile industry these devices are known as vacuum extractors. These devices can reduce the moisture content of a 65% polyester/35% cotton fabric from 60% to 36%. Nash Engineering of Norwalk, Connecticut reported that a 65% polyester/35% of cotton fabric with an areal density 0.156 kg/m^2 (trouser weight material) could by extracted so that the moisture content was reduced from 75 to 36% (5). A production rate of 7000 m^2/hr would require a 40 horsepower electrical motor motor. Accordingly, it can be determined that 75,000 Joules/kg of thermal energy are needed per kilogram of water removed. This volume compares favorably to that value determined earlier for a squeeze roll. However in order to obtain a complete appreciation of the comparison one must keep in mind that even though a squeezer is more energy efficient, it cannot dewater fabrics to the same level as a vacuum extractor. Moreover, a vacuum extractor can be used to dewater tufted carpeting. As an auxiliary benefit, Ostervold also indicates that a softer finish is obtained when carpet enters the dryer oven with reduced moisture (5). A possible explanation is that lower moisture content entering the dryer causes fewer residual chemicals and impurities to precipitate and leave a film on the fibers.

Van der Linden, Wassink and Theusink, have recently reported on a novel technique for mechanically extracting water though the use of a pressure differential across fabrics which is on the order of 0.5 atmospheres (6). The pressure differential is developed by either throttling high pressure steam (6 atm.) or compressed air through a one-mil wide nozzle (Machnozzle). Steam is usually employed since the nozzle operates isoenthalpically, (depending on the steam condensing equipment), and the steam can be condensed with fresh, ambient make-up water to develop useful process water from 140 °F to 180°F. The device operates on a principle that is not significantly different than that of a vacuum slot. However, the theoretical limit of pressure differential that can be obtained by a vacuum slot is one atmosphere (impossible to obtain practically) while the high pressure nozzle can produce pressure differentials that are significantly greater than those produced by the vacuum extractor.

THERMAL DRYING

When ambient water is placed in an open vessel under atmospheric pressure and heated, the molecules increase their kinetic energy and a temperature is attained where the liquid vapor pressure overcomes the atmospheric pressure. We commonly call this temperature the boiling temperature and the energy necessary to convert one kilogram of water to vapor the latent heat of vaporization. At first glance, one might suspect that the thermal energy required for thermal drying is only that needed to raise the temperature of the water to the boiling point and the subsequent latent heat of vaporization. This is not at all the case since substantial energy is needed to affect drying for standard production processes.

In this section an accounting of energy consumption during drying will be presented. Suggestions for minimizing energy consumption will also be offered. First it is necessary to review the physics of drying. Most thermal drying is accomplished with either convective dryers (tenter frames) or conduction dryers (steam cans).

Physics of Convective Drying

Considerable research has shown that the moisture content is a function of drying time (Figure 1) and that drying rate of a fabric is a function of moisture content (Figure 2). Explanation of the data presented in Figure 2 follows. If the fabric is heated at the surface, the moisture movement within the fabric must occur at a rate commensurate with that needed to maintain a saturated condition at the surface of the fabric. All drying occurs at the surface and the drying rate is governed by the rate of heat transfer to the surface of the fabric. Hence the vaporization rate balances the rate of heat transfer and the temperature of the saturated fabric surface remains constant. During this period the drying rate is constant. Eventually the water flow to the surface is no longer at a rate sufficient to maintain the surface at saturation. The moisture content at the end of the constant drying rate period is called the critical moisture content. After this condition is reached the fabric surface becomes only partially saturated and the plane of vaporization moves into the fabric. As this occurs a dry outer

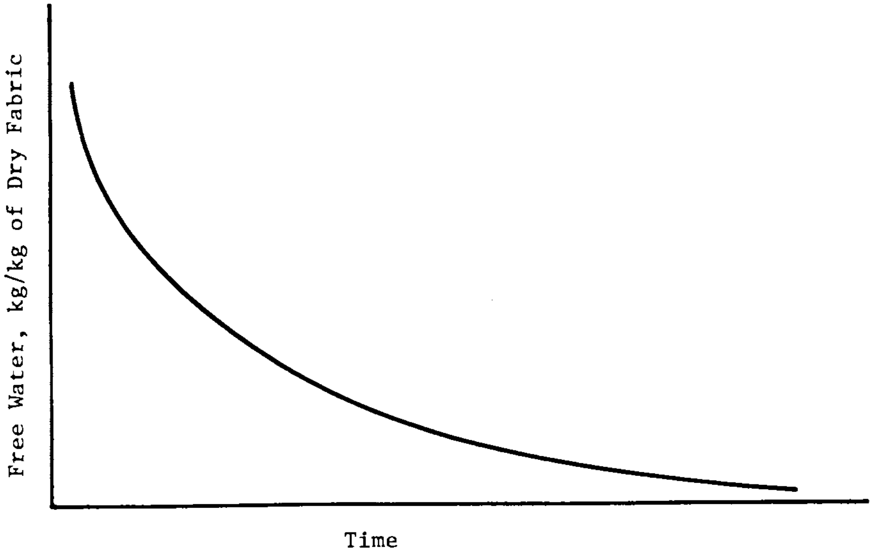

Figure 1. Free water vs. time

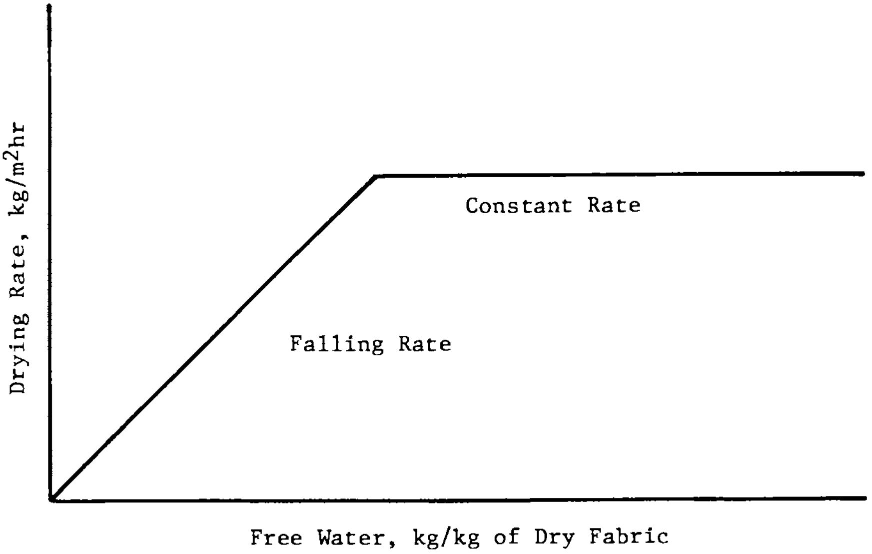

Figure 2. Drying rate vs. free water

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layer forms at the fabric surface. Since most textile materials are relatively good thermal insulators compared to water, the dry layer restricts the flow of heat to the fabric interior,thus reducing the rate of drying. The more dry the fabric becomes, the further the reduction in the drying rate. This phenomena is commonly known as the "falling rate" period. When drying fabrics to very low moisture contents, this period usually predominates in determining the overall drying time.

Beard(7) has developed a useful mathematical model of a convection dryer for studying the use of energy in a tenter frame. The model is based on a set of simultaneous differential equations which can be solved numerically to obtain fabric temperature and macroscopic moisture contents along the length of the dryer. The model considers the fabric as a moist layer of fabric sandwiched between two dry layers of fabric. Thermal energy is convected from the dryer to the external surface of the dry layer and then from the exterior of the fabric to the interface between the wet and dry layers. At the interface, the water is evaporated and diffuses as vapor through the dry layer to the surrounding hot make-up air. Assumptions in the model include:

1. The interface between the hot air and the dry layer of fabric provides negligible resistance to the water vapor leaving the interior of the fabric.
2. The internal moist layer has neither a temperature nor moisture gradient.

Enthalpy balances for the dry layers and the wet layer can be formulated along with a pertinent drying rate equation. Formulation by Beckwith and Beard results in three ordinary differential equations that describe the dry fabric temperature, the wet layer temperature and most importantly, the moisture content of the total fabric as a function of time(1). By predetermining the fabric speed through the dryer, residence time can be converted to dryer length.

The enthalpy balance of the dry layer may be expressed as:

Heat in entering dry fabric + Heat added from air = Heat in dry fabric exiting + Heat conducted to moist layer

The enthalpy balance of the wet layer may be expressed as:

Heat in wet fabric entering + Heat conducted from dry layer =

Heat in dry fabric exiting + Heat in moisture exiting + Heat in vaporized moisture

Treybal shows that the drying rate r, (kg of water/m^2 min) can be defined in terms of the heat transfer rate(8)

$$r = \frac{H}{Ks} (Y_2 X/X_c - Y_1)$$

The mathematics of the above physics can be formulated as

$$\frac{d\,Te}{d\,t} = \frac{H}{3600} \quad \frac{Ta - Te\ ({}^{H}1/H)\ (Te - Ti)}{Cpf}$$

$$\frac{d\,Ti}{dt} = \frac{H_1}{3600} \quad \frac{(Te - Ti + {}^{H}/{}^{H}1)\ ({}^{dx}/dt)}{Cpf + Cpw\ x}$$

$$- 3600 \quad \left(\frac{dx}{dt}\right) = ({}^{H}1/1)\ ({}^{Y}2 - {}^{Y}1)\ x^{a}$$

The equations contain emperically determined parameters, H, H_1, B, and a. They can be determined by curve fitting the model output to experimentally measured fabric temperature profiles.

Energy Requirements for Convective Drying

Hebrank and Brown have reported an audit of energy use in a tenter dryer oven(2). Their study shows that the energy consumption must be divided into that needed for evaporating water, heating make-up air, and heating cloth. Make-up air is the air which must replenish that exhausted from the oven after it becomes moisture laden. This is necessary if a satisfactory production rate is to be maintained for as the humidity of the tenter environment increases the productivity decreases. It is generally accepted that 24 kg of air are needed to remove 1 kg of water and another 1.75 kg of air are needed for every kg of resin-treated fabric. Summarizing the energy need requirements for drying a fabric weighing 0.2 kg/m^2 and entering the dryer at 35% moisture content, we have:

Water Evaporation	2.70×10^6 J/kg
Cloth Heat	0.93×10^6 J/kg
Make up Air	3.95×10^6 J/kg
	7.58×10^6 J/kg of water

However, if the entering fabric moisture level is 100%, the energy requirements per pound of evaporated water are:

Water Evaporation	2.70×10^6 J/kg
Cloth Heat	0.93×10^6 J/kg
Make Up Air	3.50×10^6 J/kg
	7.13×10^6 J/kg of water

At first glance, it appears that the 100% moisture content fabric uses less energy for drying than the 35% moisture content fabric. But there is a fault in this observation since the energy requirements are based on water and not fabric. That is, for the

35% moisture content fabric we need 0.35 x 7.58 x 10^6 J/kg of water or 2.65 x 10^6 J/kg of fabric while the 100% moisture content fabric needs 1.0 x 7.13 x 10^6 J/kg or 7.13 x 10^6 J/kg of fabric. It can be seen readily then that the lower the moisture content of the fabric entering the dryer, the lower the total energy use. This principle will be discussed further in the section on drying economics. Now that general physics and its applications have been reviewed for convective drying in a tenter frame, it is now possible to suggest methods which will result in energy conservation. Beckwith and Beard show that increasing the heat transfer coefficient between air and the dry fabric can lead to the use of lower air temperatures(1). Lower air temperatures will result in signficantly lower make up air energy requirements. The heat transfer coefficient may be increased by implementing air impingement and subsequent "through drying" techniques. Through drying is the process of drying a wet, porous medium by the direct passage of hot air through its bulk. It differs from simple convective drying in that the drying medium is forced through the fabric to enhance the mass transport phenomena. Accordingly, the make up air requirements can be expected to be lower. Moreover, the temperature of the air can be lower which directly results in energy savings. The underlying physics of through drying is based on the fact that the intimate contact between fabric moisture and hot air not only furnishes a greatly increased area for heat and mass transfer but also provides a shortened transfer distance for evaporating the water. Wedel and Chance have reported a thorough analysis of through drying of paper(9). The essence of their analysis can be used to show that paper weighing 0.2 kg/m^2 can be dried using 3.3 x 10^6 J/kg of water when the initial moisture content is 250% and the final moisture content is 50%. These moisture contents are not in line with those common to textile processing and it is suggested that their analysis be executed with common textile parameters. Nonetheless, through drying should be considered for energy conservation during textile drying.

Another technique for conserving energy involves exhaust control to maintain the dryer humidity at an optimum level. Earlier, it was stated that about 24 kilograms of air are required for every kilogram of water removed. Typically exhaust systems in ovens are set to evacuate a constant volume of make up air. However this procedure can be costly in that certain operating conditions (i.e., low incoming air moisture content) allow drying at lower flow rates. Accordingly, it is advantageous to monitor the effluent moisture content and vary the flow rate of the exhaust fan. Moreover, when fabric styles are changed or the throughput rate is changed, the exhaust requirements will vary. Programmed exhaust can also result in energy savings. For example .if the exhaust dampers are shut during a start up period, the oven will heat up faster and can result in fuel consumption savings of 75% during warm up. Tenter frame environments should not be purged until the exhaust air reaches an absolute humidity of 10% or it is laden with smoke in excess of 1/2% by weight or explosive vapors are concentrated to 25% of their explosive limit. In summary, Figure 3 summarizes the energy requirements for a tenter as a function of humidity and incoming moisture content.

Physics of Conduction Drying

Textile materials are frequently dried on steam cans. These devices consist of hollow metal cylinders heated by pressurized steam. The steam pressure is 3-6 atmospheres. This drying method is relatively energy efficient since a high heat transfer rate is possible when wet fabric makes firm contact with the steam can. Although in most U.S. textile mills steam is supplied directly from a boiler, the steam can be obtained from the exhaust of an electrical generator turbine. This cogeneration is readily adaptable to the textile industry since finishing mills are usually located proximate to dry processing mills where electrical energy is used mostly.

Nissan and Hansen(10) investigated the transient heat transfer and subsequent water removal on a cylinder dryer. Their proposed physics is based on a heat balance relationship:

$$k_x \frac{\delta^2 t}{\delta_x^2} + k_y \frac{\delta^2 t}{\delta_y^2} + k_2 \frac{\delta^2 t}{\delta_z^2} - V\rho C \frac{\delta t}{\delta z} = 0$$

At this point it is important to note that this equation assumes that the controlling mechanism for heat transfer is conduction. Later, Hartley and Richards(11) developed a diffusion model for the hot surface drying of sheet materials.

Returning to the Nissan and Hansen model, they use a finite difference numerical analysis model to determine both the temperature profile of a sheet material and the subsequent water removal as it passes over the cylinder. Their experimental results match well with the predicted values. However, their experiments were limited to a cylinder surface temperature of 93.3°C. Accordingly, the maximum vapor pressure of the evaporated water is less than one atmosphere. The diffusion model advanced by Hartley and Richards is in close agreement with experimental work of Dreshfield(12). However, the boundary conditions are still relatively uncertain since the convective flow region outside the sheet is relatively unknown. Later work by this author studies this convective flow.

ECONOMICS OF DRYING

The energy required for dewatering is usually derived from one of four sources: electricity, coal, fuel oil or natural gas. Sometimes propane is substituted for natural gas. Squeeze rollers, pads, mangles and vacuum slots all use electrical energy. Steam cans and the Machnozzle use steam which is

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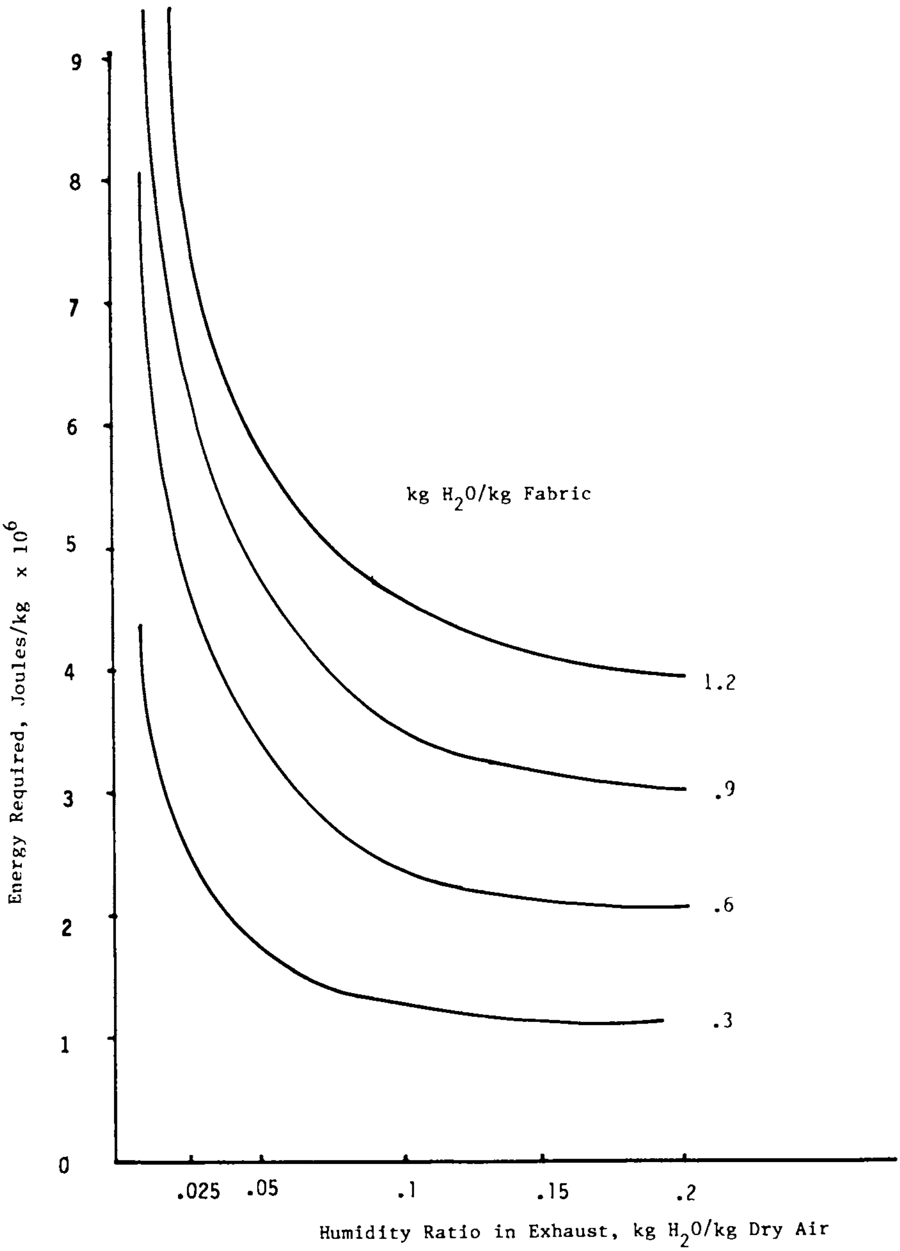

Figure 3. Effect of predrying and exhaust controls on dryers

generated in boilers fueled with either coal, gas, or oil; tenter frames are usually direct fired with clean burning gas. Based on the following common prices for fuel in 1978 the energy costs for drying by the different methods described in the text can be determined.

Coal generated steam:	4.53×10^8	Joules/dollar
Oil generated steam:	3.5×10^8	Joules/dollar
Electrical Energy:	0.9×10^8	Joules/dollar
Direct Fired Gas:	7.54×10^8	Joules/dollar

The value for electrical energy is an actual value for "energy at the socket." Using this value, the cost for removing water mechanically may be readily determined. If we consider a fabric which has been squeezed from 150% moisture content to 75% moisture content, the cost is 1.78×10^{4} dollars per kilogram of water removed. If the fabric is now dried to 0% moisture content in a tenter frame, the remaining water is removed at a cost of 0.01 dollars per kilogram of water removed. The vast difference in cost of water removal depending on technique should be noted here. Summarizing the costs for a 0.2 kilogram/m^2 fabric which is to be dried by a combination of squeeze rollers, vacuum slot and tenter oven:

150% moisture content
or
0.3 kilogram/m^2 of water to be removed

0.3 - 0.15 kg	--	2.57×10^{-5} dollars	squeeze rollers
0.15 - 0.072 kg	--	1.0×10^{-6} dollars	vacuum slot
0.072 - 0.0 kg	--	7.2×10^{-4} dollars	thermal removal
		7.48×10^{-4} $\frac{\text{dollars}}{\text{m}^2 \text{ of fabric processed}}$	

This total value is only 3% greater than the value for just thermal removal, hence we can state that thermal removal costs determine essentially the cost of drying. However, since mechanical methods are relatively cheap they should be exercised to the fullest extent. For instance if our fabric enters the tenter frame at 100% moisture content 18.9×10^{4} dollars/m^2 of fabric processed is the cost of drying.

GLOSSARY

a, B = Experimentally determined constants

c = Specific heat

C_f = Specific heat of dry fabric, J/kg^{o}K

C_{pw} = Specific heat of water, J/kg^{o}K

H = Heat transfer coefficient between air and dry surface,

H_1 = Heat transfer coefficient between wet and dry fabric surfaces, W/m ^{o}K

Ks = Experimentally determined constant

K = Thermal conductivity

T_a = Dryer air temperature, ^{o}K

T_e = Fabric surface temperature, ^{o}K

T_i = Temperature of wet fabric, ^{o}K

t = Temperature

V = Velocity of fabric in direction Z

X = Moisture content of fabric

X_c = Critical moisture content of fabric

x = Distance through thickness of fabric

y = Coordinate direction or distance in cross direction

y_1 = kg of water/kg of dry air of the dryer humidity

y_2 = kg of water/kg of dry air at air-water interface

z = Distance in direction of fabric travel

ρ = Density

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Literature Cited

1. Beckwith, W.F., and Beard, J.N., Jr., A Scheme to Assist in the Evaluation of Tenter Frame Dryer Performance, ASME publication 78-Tex-4, Trans. ASME J. Eng. for Ind. 1978.

2. Hebrank, W.H., and Brown, W.C., Means to Reduce Fuel Requirements of Textile Finishing Tenter Dryers, American Association of Textile Chemists and Colorists, 1974 National Technical Conference, New Orleans, Louisiana.

3. Lyons, D.W., and Vollers, C.T., The Drying of Fibrous Materials, Text. Res. J. (1971) 41, 661.

4. Kuppers, J.R., Text. Res. J. (1961) 31, 490.

5. Ostervold, J., Bottleneck at Drying, Text. Ind. (April 1966) 130.

6. Van der Linden, H.J.L.J., Wassink, J.G. and Theusink, C.A., Anwendung der Schallstromung von gasen and Dampfen in der Textileveredlung, Mell. Textilber.(1976) 53, 57.

7. Beard, J.N., Jr., More Efficient Tenter Frame Operations Through Mathematical Modeling, Text. Chem. Color. (1976) 8, 30/47.

8. Treybal, R.E., "Mass Transfer Operations", 2nd Ed., McGraw Hill, New York, 1968.

9. Wedel, G.L., and Chance, J.L., "Analysis of Through Drying", Beloit Corporation, Beloit, Wisconsin.

10. Nissan, A.H., and Hansen, D., Heat and Mass Transfer Transients in Cylinder Drying: Part I, Unfelted Dryers, A.I.Ch.E. J. (1960) 6, 611.

11. Hartley, F.T., and Richards, R.J., Hot Surface Drying of Paper, The Development of a Diffusion Model, TAPPI (1974) 57, 157.

12. Dreshfield, A.C., and Han, S.T., TAPPI (1956) 39, 449.

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Effective Use of Textiles for Energy Conservation

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Every major industry has addressed itself to the conservation of energy and the most efficient and economical use of new and existing energy resources. The textile industry has identified many ways in which energy consumed by fiber processing and fabric finishing may be lowered (see other chapters of this book). However, little information exists on how textile products may be used most effectively for conserving energy, and how thermal comfort indoors is related to the use of textiles in energy-conserving strategies. At present, clothing and textiles are designed primarily for aesthetic or non-thermal benefits rather than for conserving energy. The thermal comfort of individuals in residences, office buildings, and other indoor environments, however,significantly affects the maintenance of thermostats at temperature levels recommended for conserving energy.

Textiles used in direct (apparel) or indirect (bedding) contact with the body can prevent heat loss in winter or insulate from heat gain in summer so that less energy is required in heating, cooling, and humidifying systems to optimize the thermal comfort of individuals. In addition, non-contact items (draperies, wall coverings, and floor coverings) help contain warmed or cooled air in buildings.

The thermophysical properties of textiles--thermal conductivity, heat transfer (conduction, convection, and radiation), and specific heat--are important to the overall thermal response and insulation provided by thermally functional textile materials. Each textile product used indoors contributes to the overall thermal comfort of occupants of rooms and buildings and the thermostat settings employed (Figure 1). To assess the effects of textiles on thermal comfort indoors, researchers need to monitor the room and building properties that are related to thermal comfort. Current techniques and knowledge for identifying the most effective use of textiles indoors for saving energy will be described. Some specific areas needing additional research will also be mentioned.

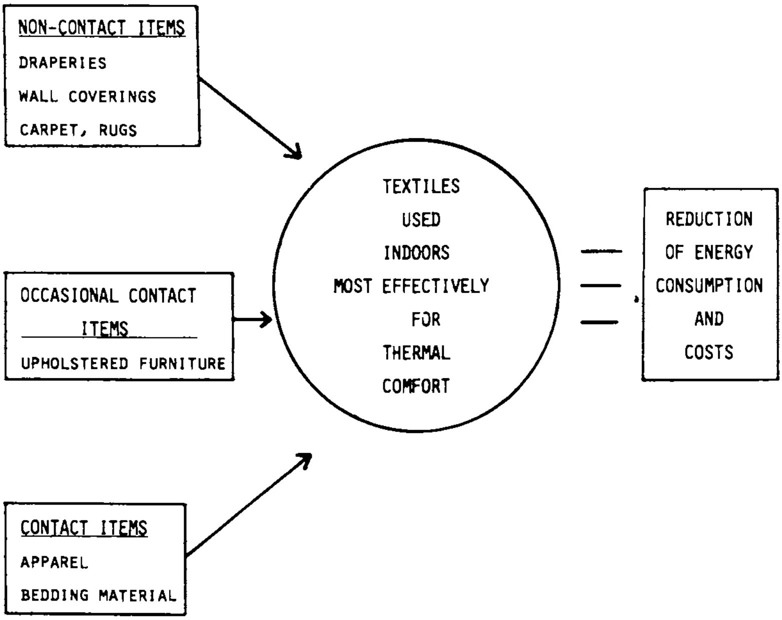

Figure 1. Optimizing textile usage indoors for energy conservation

Thermophysical Properties

Thermal Conductivity. The most frequently investigated thermophysical property of textiles is thermal conductance, or U, the heat flux without convection transfer (usually expressed as calories/meters^2 x seconds x °C), or its reciprocal, thermal resistance. Thermal conductivity, or k, is thermal conductance normalized with respect to the heat flux per unit degree temperature across unit thickness of the material (expressed in calories/meters x seconds x °C). Many studies have demonstrated that thermal conductance primarily depends on fabric thickness and air present in the material; however, the conductivity of air accounts for the greater part of the conductivity values observed (1, 2, 3, 4). Although the total conductance or resistance of the fabric may be readily measured, it is quite another matter to predict from theory the conductance or resistance of fabrics because of the variability of the amount of air trapped in the textile (5). However, some recent studies have successfully employed various models for predicting conductance of textiles with convective and non-convective heat transfer (6-11).

Theoretical values of the effective thermal conductivity of polyester fabrics (6) (estimated by an expression developed for fibers placed in parallel with each other surrounded by a known amount of air and vice versa) agreed well with line heat source measurements of the thermal conductivity of fabrics varying in thickness, construction, and fiber content (7). These results also indicate that the thermal conductivity of fabrics in directions parallel to the surface is greater than that perpendicular to the surface, especially for filament yarn; the thermal conductivity of woven fabrics in directions parallel to the warp yarns, which were arranged more closely, was greater than in directions parallel to the filling yarns (7).

The line heat source method was also used to measure the thermal conductivity of wet fabrics parallel to the warp yarns and normal to the fabric surface using layers of fabric (8). The relationship of the thermal conductivities of fabrics and volume fractions of water in the interfiber spaces was expressed by a quadratic curve when the heat flow was normal to the fabric surface and by a straight line when the flow was parallel to the warp yarns. Except for hairy wool fabrics, the thermal conductivity of various wet fabrics may be calculated from the equations of Naka and Kamata (8). An earlier investigation used an environmentally controlled room as a periodic heat source, and observed conductivities of 1-2 x 10^{-4} cal/cm-sec °C for cotton, linen, and wool fabrics, and changes to 2-10 x 10^{-4} when the water content of these fabrics were increased (9). After correcting for anisotropic effects, good agreement between actual conductivity measurements of wool fabrics and those calculated from a mathematical model of a random arrangement of fibers was observed.

The model consisted of a regular arrangement of three sets of parallel cylinders, each set being orthogonal to the other two (10).

Heat Transfer. Values observed for heat transfer by conduction and the overall coefficient of heat transmission of flexible plastic sheets reinforced with plain woven fabrics demonstrated that a mathematical model was useful for prediction of the conductivity of the plastic sheets; however, bulk density of the fabric had no effect on the conductivity. It was also found that the overall coefficient of thermal transmission of the plastic sheets insulated by woven fabrics depended largely on the conductivity of the insulating fabrics (11).

Under conditions of free convection, a linear relationship was observed between warmth retention and fabric thickness of rayon and cotton knits with different constructions (12). In a recent study, basic equations for heat transfer by free convection in fiber assemblies were developed. They consisted of three partial differential equations of continuity, momentum, and energy and were analyzed by boundary layer approximation and dimensional vector techniques. Temperature distribution in the fiber assemblies became linear with development of convection (13). Satisfactory agreement was found between predictions from a model and experimental measurements of the rate of heat flow through a wool fabric during changes in its moisture regain caused by changes in the relative humidity of the surrounding air. The "buffering efficiency," defined as the ratio of effective sorption heat (i.e., the area under the heat flux-time curve) to the total sorption heat, was in good agreement with the experimental value (14).

It has been known for some time that the color of fabrics and the types of dyes used can be important factors in determining the solar reflectance of fabrics (15, 16). However, color of fabrics in apparel has no effect on the loss of body heat since the color of a fabric has a small effect on its surface emittance (16). Other factors such as fiber orientation and length, yarn twist, and fabric structure also influence the infrared and visible reflection properties of various fabrics (17). In a recent study, the various radiant properties of textiles measured at the peak emission wavelength of sunlight (0.6 μm), were found to approach constant values of absorptivity (0.67), absorptance (0.33), transmissivity (0.0), and reflectivity (0.33) at infinite superficial density (3).

Specific Heat. The specific heat of textiles, particularly wool, has been the subject of recent investigations. For moisture contents above the fiber saturation point of wool, reduced, supercontracted, and chemically modified wool fabrics exhibited endothermic peaks at -30 to 0°C that resulted from the heat of fusion of absorbed water. In that temperature range, a significant increase in the specific heat of the wool fabrics was also observed. Below the fiber saturation point, the specific heat of wool increased only moderately with increasing temperature; no endothermic reactions were observed below a moisture content of 22.7% (18, 19). An equation which relates the specific heat of moist wool at a given moisture content to the specific heat of water and water content of wool was proposed to explain experimental values obtained for specific heat of most wools having varying water contents. This investigation also suggested that a modified Clapeyron-Clausius equation (which relates changes in vapor pressure to temperature through the latent heat of vaporization of a material) is applicable only for temperature-invariant values of the differential heat of sorption of wet wool fabrics (20).

In addition to wool, other hygroscopic textile materials such as cotton and linen underwent a threefold increase in their specific heat at constant vapor pressure. The relatively high specific heats derived from equations in the study, which are considered to represent those incurred in actual use of the hygroscopic textiles, explain the well-known buffering action of these fabrics toward sudden changes in indoor or outdoor temperatures (21). A compilation of the specific heat of a variety of textile fibers at 20-200°C indicates that considerable variation in the values of this thermophysical property occurs with different fibers (e.g., a value of 0.157 for glass and 0.49 cal/g.°C for Nylon 66 are reported), and that additional research is needed to establish the extent to which specific heat affects the characteristics of thermal transmission in textiles (22).

Instruments for Measuring Thermophysical Properties

Many investigators have proposed and utilized instrumentation that measures the thermophysical properties of textiles. One fundamental classification system for such instruments is based on the state of the heat flow involved: (a) constant temperature, (b) rate of cooling or warming, and (c) heat flow meters or disks (23). Other factors that must be considered with such instruments include the variables that are actually measured and controlled, provision for free or forced convection, simultaneous moisture transfer, and variability of air velocity. Table I lists representative instruments and the conditions and parameters with which the thermal properties of textiles are measured.

The guarded hot plate is a standard instrument for measuring the relative thermal resistance of textiles as heat flows from a heated plate in contact with the textile and dissipates into still air at a lower ambient temperature via radiation, conduction, and convection. By design, it minimizes errors due to edge heat losses and validates the total quantity of heat flowing through the specimens. Convection and surface radiation can be controlled by use of a hood (24). Simpler devices such as the Reeves warmth tester and a chamois-covered copper cylinder also measure thermal

Table I. Representative Instruments that Measure Thermophysical Properties of Textiles

Instrument	Measuring Technique	Thermophysical Properties Measured	Other Properties Measured or Controlled	References
Guarded hot plate	Equilibrium temp.	Resistance	Convection, radiation	24
Reeves warmth tester	Equilibrium temp.	Resistance	None	25
Chamois-covered copper cylinder	Equilibrium temp.	Resistance	None	26
Togmeter	Heat flow disks	Resistance	Convection, radiation, temperature	27
Fiber heat sink	Equilibrium temp.	Axial conductivity	Radiation, convection, emissivity	29
Warmth tester	Equilibrium temp.	Resistance	Air velocity, convection, radiation	31
Cenco-Fitch	Rate of heating	Conductivity	Convection	2
Heat transfer apparatus	Heat flux	Conductivity	Convection, radiation	35
Thermal moisture tester	Rate of heat and moisture transfer	Thermal efficiency	Relative humidity, temperature	36
Optical integrating sphere	Photovoltaic cell	Absorptivity, reflectivity, transvissivity	Total radiation, emissivity	3
Quartz tube heater	Heat flow	Emissivity	Resistance	3
Adiabatic calorimeter	Temperature/heat input	Specific heat	Heat of fusion of absorbed water, temperature	19

resistance but do not attempt to control the atmosphere in which the instrument is placed or to compensate for edge effects (25, 26). The thermal transmission apparatus (togmeter) described by Clulow and Rees (27) uses a heated plate and standardized conducting disks in series with the specimen to compute the heat flow through the textile. Thermal resistance can be measured by using one or two plates, thus simulating various modes of fabric end use.

Other approaches for measuring thermal resistance or conductivity of fibers and fabrics include the use of calorimetry (28), thermal flow through a heat sink of known emissivity (29), immersion of fibers or fabrics in liquids of known thermal conductivity (30), and measurement of the rate of cooling of textiles or insulating materials by a Cenco-Fitch apparatus (2).

There are few studies on instruments that measure thermal resistance of textiles while varying convection and/or air velocity. An early example of these devices employed a refrigeration unit and measured the thermal efficiency or resistance of textiles at air velocities up to 13 mph (31). Later studies measured the thermal resistance of knits under free and forced convection (32, 33); some also used bicalorimeters to simulate the shape of the textile during actual wear (34).

Behnke and Seaman (35) have designed equipment which measures the conductive, convective, and radiant heat flux through textiles. However, their instrumentation was designed for testing protective clothing to high temperature exposure and may not be useful for assessing thermal characteristics of textiles under normal end-use conditions.

Another apparatus based on the rate of cooling or warming has the provision for measuring moisture transport through textiles simultaneously with thermal diffusion and is considered by its developer to be superior to other instruments which neglect moisture transport (36).

In a recent, comprehensive investigation, an optical integrating sphere was used to measure the effects of radiation and its component parts, absorptivity, reflectivity, and transmissivity, of a fabric. Emissivity of the textile wrapped around a heated brass cylinder was measured by thermoprobes in an evacuated environment (3). The specific heat of textiles is usually measured with adiabatic calorimeters; other thermal characteristics such as heat of fusion of absorbed water in fibers were also measured by this technique (19).

Clothing and Thermal Comfort

The thermal and nonthermal aspects of clothing comfort have often been investigated. Several excellent books on these subjects emphasize the physiology, psychology and aesthetics, thermophysical properties, and environmental conditions associated with thermal comfort (23, 37, 38, 39).

Physiology. Research by Goldman and others at the U. S. Quartermaster Corps focuses on the relationship between body physiology and clothing comfort. Although much of this work is concerned with garments worn in extremely cold or hot outdoor environments, many of the basic considerations are applicable to indoor environments. The effectiveness of clothing assemblies has been evaluated by use of a "sweating" copper mannequin. The clothing insulative value or resistance (clo) and evaporative heat transfer from the skin (i_m) are measured and related to the overall protection that garments afford (40). A classic heat balance equation for storage of heat in the human body (ΔS) that relates metabolic heat production, solar heat load, radiant and convective heat exchanges, and evaporative heat loss was used in these studies (41). The effectiveness of clothing for maintaining thermal comfort in extreme climatic conditions (40) was examined by measuring and then varying different physiological factors in wear tests and tests in a controlled chamber.

Direct evaluation of the convective heat transfer coefficient (h_c) of subjects clothed in undergarments and socks (normal ventilated environment) was achieved by observing the sublimation rate of naphthalene balls uniformly positioned three centimeters from the body surface. Equations were developed for prediction of h_c as a function of metabolic activity and posture, calculation of average skin temperature, and estimation of maximum evaporative heat losses from the body (42). In another approach, the coefficients of dry heat transfer at varying wind speeds for nude and clothed sectional mannequins were determined (43). At air flow rates above 2 m/sec, percentage contributions of individual body sections to total heat transfer remain constant for the nude and clothed mannequin, yet increased for normally uncovered units such as the face and hands. Generally, the ratio of total heat flow for the nude to clothed mannequin increased with air flow.

Breckenridge has investigated the effects of body motion on convective and evaporative heat exchange through various designs of clothing; his physiological study involving a walk-rest-walk routine for subjects clothed in different garments demonstrated that varying amounts of body heat storage attributed to garment design and form-fitting characteristics could not have been predicted by use of a mannequin (44). In another study, the importance of the "bellows ventilation" effect of clothing was stressed and changes in temperature, relative humidity, and heat flow on the skin and inside clothing were used to demonstrate the effect of forced ventilation on changing wearer microclimate during walking (45). Heat flux was measured over the body surface of clothed and unclothed persons under conditions of heat equilibrium and varying cooling intensity, and was related to actual values for heat-loss rates due to convection and radiation (46).

Mecheels has reviewed his extensive comfort investigations on thermophysiological and psychrometric comfort ranges of

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clothing systems (47, 48, 49, 50). The latter term or concept is defined as the difference between $T_{a_{max}}$ and $T_{a_{min}}$ for a particular clothing system, that is the difference between a maximum ambient temperature at which the body/clothing system will just succeed in keeping core temperature constant under not quite comfortable, yet bearable, conditions even if heat production is taken into account and a minimum ambient temperature at which a person with a defined minimum heat production will just not yet feel cold. $T_{a_{max}}$ is dependent on the ambient relative humidity and on the total thermal and moisture resistance of clothing assemblies (R_c and R_e). Mecheels suggests that the useful range of a clothing system is optimized by a high moisture passage index $i_m=f(R_c/R_e)$ and a high thermal insulation value that decreases greatly with increased activity of the wearer. $T_{a_{min}}$ is dependent only on the total thermal resistance of the assembly. Textile properties of R_c and R_e for multilayers of clothing were determined by use of a Hohenstein skin apparatus in which the thermal and moisture resistance values can be calculated from the slope of a plot of reciprocal conductive and evaporative heat flux versus number of clothing layers. Mecheels' copper mannequin which has flexible limbs and thus the capability of standing, sitting, lying, or walking at variable speeds, was used to determine these resistance values under dynamic conditions.

There have also been a few studies on the physiological aspects of thermal comfort of blankets and bedding materials. The effects of bed linens made of cotton, cotton/polyester nonwoven blankets on physiological aspects of thermal comfort were compared. With the aid of periodic measurements on the depth of sleep and other physiological factors, Nesswetha concluded that construction of the fabrics, not their fiber type, was the most significant factor in determining thermal aspects of bedding microclimates (51). The study was criticized on the soundness of its physiological approach, but the original investigator justified his results as being useful to consumers and textile manufacturers, if not to physiologists (52).

Psychology and Aesthetics. The subjective or psychological scaling of comfort assessment has been discussed and reviewed by Hollies (53). A subjective linear scale containing 13 descriptors for thermal comfort over the range from extreme cold to extreme hot is described. The importance of clothing contact with the skin in relation to subjective comfort ratings is also stressed. The correlation of such ratings to measurement of dynamic surface moisture was demonstrated by color changes in fabrics impregnated with cobaltous chloride (53). Fuzek found most coefficients of correlation between subjective comfort evaluation and objective test results for wear trials with undershirts were insignificant and only significant between subjective perspiration/absorption assessments and measurement of water of imbibition (54). More recent studies, however, claim that the cold or warm feel of fabrics can be estimated by measurement of rate of cooling or heat flow (55, 56).

Thermophysical Properties. Several investigators have focused their work on evaluation of the thermophysical properties of clothing assemblies and either related the results to mannequins or wear trials or discounted the need for such trials and elaborate models. Total thermal resistance of a clothed body to heat transfer from the body to surrounding air was considered to be the sum of three properties: thermal resistance of the textile, thermal resistance to heat transfer at the textile surface, and thermal resistance of the air interlayer. Relationships between thermal resistance of clothing assemblies, air permeability, wind speed, and assembly thickness were also explored (57). A method for calculating the effects of wind speed on thermal resistance of clothing claims to be as reliable as tests that use mannequins (58).

Another study has classified air between layers of fabrics in clothing assemblies into thin, closed layers and relative thick and extensive layers, and related the thermal resistance of an assembly to the open-air layer, the air permeability, and the air velocity (59). Shivers et al. used a gas tracer technique to demonstrate the importance of microclimate air exchange in thermal comfort of clothing assemblies (60).

Several investigators have described or proposed instruments that measure the heat and moisture transfer characteristics of clothing assemblies. One group of instruments (61, 62, 63, 64) consists of bicalorimeters or water-filled copper cylinders, which attempt to simulate wearer conditions while measuring dynamic changes in these properties. Other approaches discount the need for elaborate instrumentation or consideration of moisture transfer and relate the thermal comfort of an individual just to thermal resistance of the fabric (65) or use instruments having the capability of measuring moisture and heat transfer under a wide range of environmental temperatures (66, 67). Rowlands, however, has constructed an apparatus for measuring the thermal conductivity of blankets under conditions simulating end use that also takes water vapor transfer into account (68).

Spencer-Smith critically and thoroughly reviewed the physical basis of clothing comfort in four recent papers and discounted much of the previous work on heat and water vapor transmission through clothing assemblies (69, 70, 71, 72). In the first paper (69), he focuses on the special properties of hygroscopic fabrics such as linen and wool and points out that previous studies demonstrate that their buffering action affords comfort in moving from warm dry atmospheres to cold damp ones

(73). In the second paper (70), he presents equations for convective and radiative heat transfer, and for natural and forced convection which can be used for calculation of heat loss through dry clothing assemblies. In the third paper (71), he discusses water vapor transfer through dry clothing assemblies and stresses the complexity of such measurements and the necessity of considering factors such as changes that occur in natural convection from the outer clothing surfaces when there are changes in the flow of heat and moisture. In the final paper (72), he deals with the passage of heat and water vapor through damp clothing assemblies and calculates the resistance of such assemblies to total heat transfer by a method of successive approximations. He also observes that no transfer of liquid water occurs between wet and dry fabrics that are in contact until the excess moisture content of the wet fabric exceeds 75%.

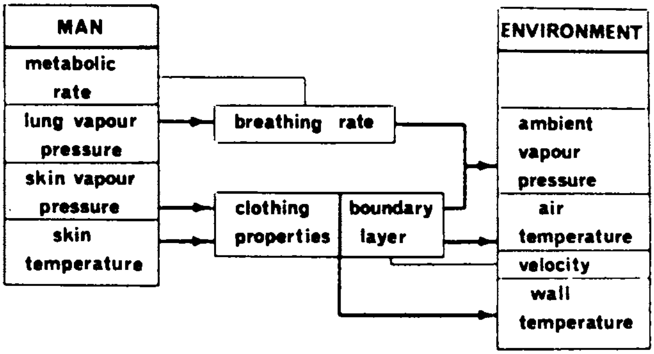
Environmental Conditions. The last area of discussion concerns those studies that emphasize environmental factors indoors and their interrelationship with clothing. Fanger's multivariate equation for predicting thermal comfort indoors, which he defines as thermal neutrality, is based on statistical analysis of 1,300 Danish and American subjects and consists of six parameters: metabolic activity of occupants, clothing insulative value (clo), air temperature, mean radiant temperature, relative humidity, and air velocity (38, 74). An instrument based on these parameters and the statistical analysis is available (Figure 2); a reading for the parameters is integrated and the percent of occupants satisfied with the thermal environment is displayed.

Burton has derived an equation for preferred air temperature indoors (T_a), which is expressed as a function of body heat generated minus external mechanical work, heat lost by evaporation of water, and thermal resistances provided by air boundary layers on the outer surface and clothing layers (75). His concept of the interrelationship of persons and their indoor environment by heat transfer at the skin is straightforward and useful (Figure 3).

Development of thermal comfort standards for commercial and residential dwellings has taken place over the past fifteen years and has been sponsored by ASHRAE (American Society of Heating, Refrigeration and Air-Conditioning Engineers). In a recent study, Rohles and Nevins (76) define new comfort standards, termed a modal comfort envelope,that they derived from the distribution of thermal sensations of 1,600 subjects at a variety of combinations of temperature and relative humidity. Fanger and co-workers have designed an environmental chamber suitable for conducting thermal comfort studies under steady state and dynamic conditions (77). The chamber has several important features: the capability of maintaining uniform air and mean radiant temperatures by means of a unique floating chamber structure with low thermal capacity; uniform flow of room air; and uniform temperature of air in both horizontal and vertical planes of the test room. Fanger has also

Atkins Technical Inc.

Figure 2. Comfytest meter



ASHRAE

Figure 3. Heat transfer system at skin (75)

determined the preferred air temperatures at different clothing insulative values (0.6 clo at 23.2°C and 1.15 clo at 18.7°C), and demonstrated that mental performance was equivalent under these two conditions (78). Finally, a Federal Energy Administration study recommends wearing various types of sweaters in cold weather in order to provide thermal comfort with temperature setbacks from 2 to 5°F. Fuel-cost savings of 3% per degree lowered on the thermostat are assessed (79). However, garment constructions necessary to achieve optimum setbacks in thermostat settings were not mentioned.

Carpets, Draperies, and Other Interior Textiles

Carpets. It is generally agreed that the insulative value of carpets is primarily a function of their thickness. The type of carpet underlay and actual wear are also important in changing their thermal insulation properties (80). A recent, comprehensive study demonstrates that the thermal resistance of carpets is proportional to their thickness and pile density and essentially independent of fiber and/or yarn type. The best insulating carpet/pad combinations reduced floor heat loss up to 54% when installed on uninsulated wood floor and up to 72% when installed on uninsulated concrete slabs (81). The percent of energy saved on annual heating and cooling bills ranged from 7 to 15%, depending on the configuration of the residence and its geographical location (81).

Mathematical equations were developed to calculated the effective thermal conductivity of pile carpets. The fibers were oriented parallel, perpendicular, and on a diagonal to the carpet foundation and factors such as fineness of filaments, thread count of horizontal and vertical loops, and extent of fiber crimping were related to thermal conductivity (82).

Draperies. Several factors influence the effectiveness of draperies in reducing heat gain in the summer and heat loss in the winter. Early studies focused on heat gain and its relationship to the textile properties of absorption, transmission, reflection, openness of weave, and shading coefficient. Ozisik and Schutrum determined the effectiveness of drapes in reducing solar heat gain through sunlit glass windows by testing drapes of different materials and colors in combination with regular and heat absorbing glasses. They concluded that heat gain through a single glass with a drape could be obtained by multiplying the incident solar radiation on the glass by a solar heat transfer factor and that the solar reflectance of the drape primarily determined the solar heat gain at the window (83).

Pennington and co-workers developed equations for prediction of the total heat gain through a double glazed window with drapes as a function of the transmissivity, reflectivity, and absorptivity of individual barriers, amounts of direct and diffuse solar radiation incident upon the window structure, and the outdoor-indoor temperature differential (84). They used a solar calorimeter and pyrheliometer to measure heat transfer and radiant properties and obtained good agreement between their theoretical calculations and experimental values for relationships between radiant properties of drapes, angle of incidence of solar insolation (profile angle ϕ), and shading coefficients (84).

Yellott stressed the importance of the openness of drapes (open area between the yarn or fibers in a fabric) in determining the amount of solar heat transmitted through a drapery. He concluded that solar reflectance determines drapery shading coefficients for tightly-woven fabrics having very low openness factors, whereas solar transmission controls shading properties for fabrics having equal reflectance (85). Glass drapery fabrics were placed into nine categories on a nomograph based on their openness factor, yarn reflectance, and color; these classifications were used to select drapes for their desired indoor shading properties (86). Solar heat gain can be determined spectrophotometrically from the optical properties of drapes and window components and shading coefficients can thus be estimated without solar calorimeters or other heat flow devices (87). Petherbridge redefines the solar heat gains factor for windows and shading devices to include the effect of peak indoor temperature and a building weight or thermal reservoir response factor; the latter can be adversely influenced by the improper use of textiles to cover heavyweight surfaces (88).

Dix and Lavan conducted studies to measure the effectiveness of draperies and other indoor shading devices on the coefficient of thermal transmission, U, under winter and summer conditions (89). With the aid of two environmentally controlled chambers and thermistors located near a test window, they determined that a medium-colored drapery with a white plastic backing reduced conductive heat loss in the winter by 6-7%, and conductive and radiant (solar) heat gains in the summer by 33%. Because shades inside casements were more effective than draperies in reducing heat loss under winter conditions, they concluded that the ability of the material to block air flow was more important than other properties of the material used (89).

Specific practical recommendations are given for preventing or minimizing the "cascade effect"; this occurs by convection of air from the ceiling into the space between the curtain and the window onto the floor (90). The use of a movable wooden strip to make the curtain tight-fitting to prevent such convection is illustrated; other suggestions include the use of a relatively air-impermeable tightly-woven curtain and use of liners (90). Draperies, indoor and outdoor shading devices, and the prevention of air infiltration at windows are discussed and evaluated in a recent National Bureau of Standards publication (91). A special window and door screen fabricated from glass fiber filaments that were coated with vinyl before being woven into fabric is reported to filter out 75% of the solar heat and conserve energy in the winter by reflecting radiant heat (92).

Other Textile Interiors. There have also been a few recent studies on the thermal and optical properties of upholstery fabrics and wall coverings. The reflection and transmission properties of upholstery fabrics were determined by the use of a goniophotometer (93). Mathematical equations have been developed to show how wall hangings can save energy by confining air between walls and their coverings (94).

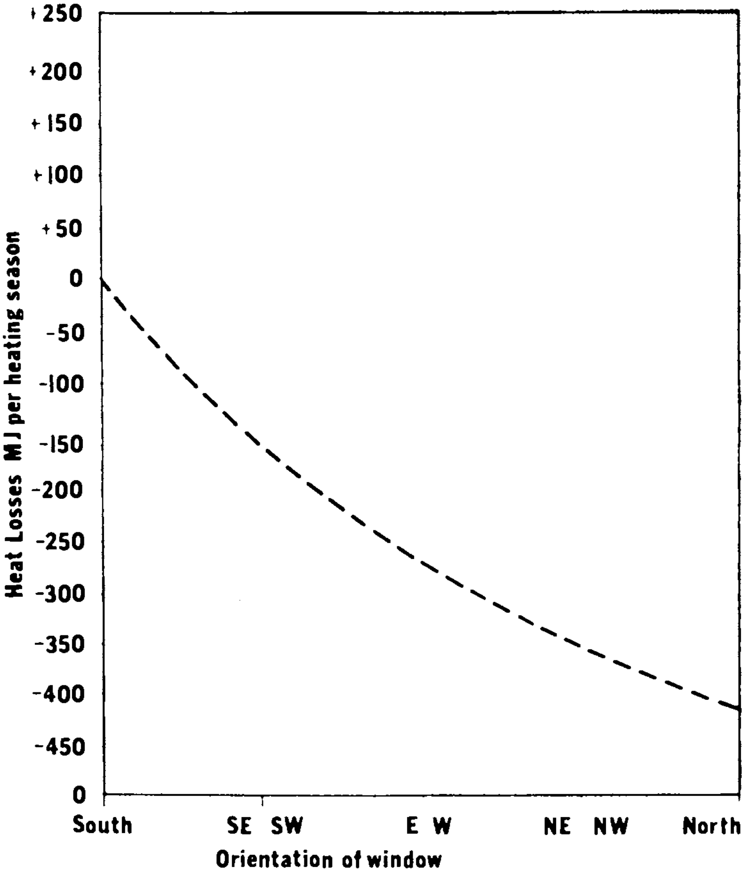
Building Science Technology

The thermal characteristics of building construction and retrofitting techniques for conservation of energy are currently very active areas of research. It is important to comment on some of these studies, insofar as they relate to assessment of the thermal characteristics of textiles used indoors. Of the numerous publications on this subject, two recent books are useful for researchers focusing on the role of textiles in providing thermal comfort indoors (95, 96).

Burberry considers the main design features for controlling thermal factors inside and outside of buildings to be site, volume and shape, location of heating and cooling sources, insulation, ventilation, steady state and dynamic thermal responses of structures, fenestration or window design, window orientation, and clothing worn by occupants (95). The effects of window orientation are shown in Figure 4, in which the net energy transfer through a one-meter square curtained window is negligible when it faces south, and appreciable when it faces north. Givoni discusses in detail subjects such as thermal effects of building materials and selection of these to adapt buildings to cold and warm climates, wetness and condensation in buildings, angles of incidence and control of solar radiation, thermal effects of roof types and ceiling heights, and prediction of indoor thermal temperatures (96).

Some specific studies on the measurement of heat losses and indoor temperatures in buildings deserve attention. In his review of the relative importance of thermal comfort in buildings, McIntyre considered that the mean radiant temperature was the most important parameter, followed closely by the "radiation vector," which is defined as the net radiant flux density vector at a given point and measures the asymmetry of the thermal radiation field in a room (97). Benzinger et al. characterized the mean radiant temperature, and asymmetric radiation fields, using a scanning plane radiometer, which maps the plane radiant temperature in a given space indoors (98).

Heat loss in buildings has been estimated by several techniques. Some recent approaches utilize instruments that relate infrared surface radiation to heat flow. Infrared thermography



The Architectural Press Ltd.

Figure 4. Net heat balance of 1 m^2 unobstructed clear glass windows, curtained at night with 17.5°C mean internal temperature for various orientations (95)

of interior and exterior temperature profiles of buildings enabled researchers to locate sites of heat loss in buildings by color-coding temperature contours of surfaces (99). Burch and co-workers assess the requirements for quantitatively estimating rates of heat loss in buildings using infrared thermography (100). With a heat flow reference pad and an infrared television system, they were able to quantitatively measure surface heat loss within 12% under still air conditions. In this technique, the actual heat flow is not disturbed as it is with conventional heat flow transducers. Both the pad and surface are observed simultaneously by an infrared thermal display, and heat flux from the reference pad is adjusted to match the heat flux from the test surface (100). Under high and moderate wind conditions, the accuracy of this technique deteriorates considerably.

Two final areas of consideration in research on heat losses in buildings are air infiltration and wetness or condensation in insulation. For a typical detached house, air leakage is believed to account for up to 40% of the heat loss (101). In tests described by Tamura, gas tracer techniques were used for measuring air exchange and pressure differences when window frames, doors, vents, fireplaces, and other openings were covered or sealed and uncovered (101). Burch and Hunt suggest measures for prevention of moisture accumulation in attics during winter and in crawl spaces during summer. These measures include placement of vapor barriers over the bare earth of the crawl space and on the warm side of the ceiling and floor insulation, and ventilation of attics and crawl spaces; such measures reduce moisture accmulation (102).

Opportunities for Research

Recent studies demonstrate that the thermophysical properties of textiles may be improved or even optimized. Such studies offer a variety of physical, chemical, and physicochemical approaches for conducting further research on the thermal characteristics of textiles that can be applied toward energy conservation.

The thermal resistance of polyamide fibers was increased by drawing them during processing; this increase was attributed to increased fiber orientation and density and a concomitant decrease in the diffusion rate of air into the fibers (103). A proposed model explains the change in thermal conductivity of semicrystalline polymers at ambient temperature as a function of their degree of orientation and crystallinity; good agreement was observed between the theoretical model and experimental values for polyethylene, polypropylene, and polyester (104). Optical fibers with a fused silica core were effectively employed to transmit solar radiation energy distances of up to 40 meters, and their use was suggested in photovoltaic cells and solar heating, cooling, and illumination systems (105). The thermal conductivity and resistance of novel fibrous materials such as carbon fibers and composites have been investigated. The thermal conductivity of carbon fibers prepared by pyrolysis of polyacrylonitrile increased progressively from 80 to 320°K (106). Technology has been developed for the production of carbon and graphite fibers and their phenolic matrix composites having low thermal conductivity and the measurement of such conductivity with special instruments (107). Sorptive composite fabrics containing activated carbon yarns had 30 to 60% greater insulative values (clo) than did fabrics normally used in apparel, and may prove useful in cold weather applications (108).

Modification of cotton textiles by chemical plating of their surfaces with cobalt (II) or nickel (II) salts produced metallized fibers and fabrics with high electrical conductivity and the capability to transport and dissipate thermal energy (109). The heat capacity of cellulose acetate fibers was increased by treatment with epoxy compounds (110).

Perhaps the most innovative and interesting product with improved thermal insulation properties is fabric made of hollow fibers with a gas and solvent inside the fibers. A decrease in temperature converts the solvent into a solid phase, thus liberating a gas and increasing the thermal resistance of the fabric (111). Although the solvents are exotic and the durability of such fabrics has not been assessed, further studies employing phase-change materials offer great potential.

For clothing assemblies, more information is needed on the insulative (clo) values of representative fiber/fabric combinations available to consumers. These clo values may then be related to thermal comfort at conservative thermostat temperatures using instruments such as the Comfytest, which has the capability of evaluating the six parameters of Fanger's thermal comfort equation (74).

Another area of research that could be profitably explored is the use of remote sensing instruments to measure surface temperatures of textile assemblies. Infrared thermovision cameras have been used to visualize temperature distributions over clothed and nude persons in order to study the transport of microorganisms by convective heat flow (112). A variety of less expensive radiometers and radiation pyrometers that are used to measure and automatically control the temperature of textiles during drying and texturing (113, 114, 115) could also assess the thermal behavior of apparel and clothing assemblies and thus elucidate their contribution to thermal comfort indoors.

Similar studies are needed on the insulative value or thermal efficiency of blankets and representative bedding materials under end-use conditions. An instrument comparable to Rowland's apparatus (68) would be useful in measuring and comparing the thermal resistance of blankets under conditions which provide specific levels of moisture transport. However, fundamental studies on both the importance of moisture transport and relative humidity of bedding microclimate with regard to thermal resistance and thermal comfort of blankets are needed.

Research on optimizing thermal characteristics of drapes should include the use of the innovative technology acquired from a knowledge of the thermophysical properties of textiles; the assessment of the relative importance of conductive, convective, and radiant properties of draperies in relation to their energy-conserving efficiency under summer and winter conditions; the variation of the amount of convective air flow and determination of its influence on other thermophysical properties; and the measurement of surface radiation of curtains and other textile interiors by remote sensing devices.

Research on the combined effects of textiles indoors would require an environmentally controlled room in which heat flux and the six variables important for thermal comfort (Fanger's equation) could be monitored and measured with appropriate instrumentation. The overall effect of textiles indoors could then be translated into their efficiency for providing thermal comfort at conservative thermostat settings.

Summary

Relatively little information exists on the most effective use of textiles for conserving energy indoors and how textile properties affect room conditions associated with thermal comfort. A review of the thermophysical properties of textiles and studies on clothing, bedding, carpets, drapes, and other textile interiors are discussed and evaluated as they relate to thermal comfort indoors. Instruments available for measuring thermal characteristics of textiles are reviewed, as well as textile and building science research related to thermal comfort. Research opportunities are summarized for improving and optimizing thermophysical properties of textiles and for measuring the combined effect of textiles on conservation of energy indoors by use of special equipment and a multivariate thermal comfort equation. The optimum benefits to thermal comfort that textiles can provide at conservative thermostat settings can then be used by textile manufacturers, businesses, and consumers to reduce the consumption of energy for heating and cooling indoor habitats.

Literature Cited

1. Pierce, F. T., Rees, W. H., J. Text. Inst. Trans. (1946) 37, T181.
2. Weiner, L. I., Shah, J., Text. Chem. Color. (1969) 1 (14), 301.
3. O'Callaghan, P. W., Probert, S. D., Build. Serv. Eng. (1976) 44, 71.
4. O'Callaghan, P. W., Probert, S. D., Appl. Energy (1976) 2, 269.
5. Slater, K., Text. Prog. (1976) 8 (3), 17.
6. Naka, S., Kamata, Y., J. Text. Mach. Soc. Japan (1973) 26, T43.
7. Naka, S., Motomura, H., Kamata, Y., J. Text. Mach. Soc. Japan (1973) 26, T34.
8. Naka, S., Kamata, Y., J. Text. Mach. Soc. Japan, Eng. Ed. (1977) 23 (4), 114.
9. Suzuki, A., Sato, A., Ohira, M., Sen'i Gakkaishi (1972) 28, 481.
10. Drummond, J. E., N. Z. J. Sci. (1971) 14, 621.
11. Horikawa, A., Sakabe, M., J. Text. Mac. Soc. Japan (1977) 30 (9), 394.
12. Korlinski, W., Malka, K., Slawinski, Z., Prezglad Wlok. (1969) 23 (9), 432.
13. Nogai, T., Nozama, Y., Narumi, Y., Sen'i Gakkaishi (1977) 33 (9), T398.
14. David, H. G., Text. Res. J. (1966) 35, 820.
15. Rees, W. H., Ogden, L. W., J. Text. Inst. Trans. (1946) 37, T113.
16. Rees, W. H., "3rd Shirley International Seminar--Textiles for Comfort," Shirley Institute, Manchester, 1971.
17. Rydzewska, D., Pr. Inst. Wlok. Lodz. (1959) 9 (2), 17.
18. Haly, A. R., J. Text. Inst. (1969) 60 (10), 403.
19. Haly, A. R., Snaith, J. W., Appl. Polym. Symp. (1971) 18, 823.
20. Walker, I. K., N. Z. J. Sci. (1973) 16, 503.
21. Spencer-Smith, J. L., J. Text. Inst. (1970) 61 (4), 194.
22. Gorlach, H., Chemifasern/Textilind. (1972) 22/74 (7), 611.
23. Fourt, L., Hollies, N. R. S., "Clothing: Comfort and Function," Marcel Dekker, New York, 1970.
24. "1977 Annual Book of ASTM Standards, Part 32," American Society for Testing and Materials, Philadelphia, Pa., 1977.
25. Am. Text. Rep. (1963) 77 (13), 33.
26. Deli, S., Durante, G., Bull. Inst. Text. Fr. (1971) 25, 939.
27. Clulow, E. E., Rees, W. H., J. Text. Inst. (1968) 59 (6),285.
28. Karlina, K. V., Tekhol. Legk. Prom. (1971) 3 (81), 26.
29. Naka, S., Kamata, Y., Yoshino, J., Sen'i Gakkaishi (1974) 30 (1), T9.
30. Shlenskii, O. F., Goncharuk, N. I., Gal'tsov, V. Y., Steklo Keram. (1969) 26 (9), 14.

31. Tallant, J. D., Worner, R. K., Text. Res. J. (1951) 21, 591.
32. Sukharev, M. I., Haase, J., Tekhol. Legk. Prom. (1970) 5, (77), 28.
33. Korlinski, W., Zesz. Nauk. Politech. Lodz. Wlok. (1970) 21, 105.
34. Torkunova, Z. A., Safonova, V. N., Teskt. Prom. (Moscow) (1975) 35, (5), 77.
35. Behnke, W. P., Seaman, R. E., Mod. Text. (1969) 50 (4), 19.
36. Cohen, G. G., Baker, C. A., Am. Dyest. Rep. (October 20,1969) 32.
37. "3rd Shirley Institute International Seminar--Textiles for Comfort," Shirley Institute, Manchester, 1971.
38. Fanger, P. O., "Thermal Comfort: Analysis and Applications in Environmental Engineering," McGraw-Hill, New York, 1970.
39. Hollies, N. R. S., Goldman, R. F., "Clothing Comfort: Interaction of Thermal, Ventilation, Construction and Assessment Factors," Ann Arbor Science, Ann Arbor, Mich., 1977.
40. Goldman, R. F., Trans. N. Y. Acad. Sci. Series II (1974) 36 (6), 531.
41. Goldman, R. F., Arch. Sci. Physiol. (1973) 27, A137.
42. Nishi, Y., Gagge, A. P., J. Appl. Physiol. (1970) 29 (6), 830.
43. Fonseca, G. F., Text. Res. J. (1975) 45 (1), 30.
44. Breckenridge, J. R., "Clothing Comfort: Interaction of Thermal, Ventilation, Construction and Assessment Factors," Hollies, N. R. S., Goldman, R. F., Eds., Ann Arbor Science, Ann Arbor, Mich., 1977, p. 153.
45. Vokac, Z., Køpke, V., Keul, P., Text. Res. J. (1973) 43 (8), 474.
46. Afanas'eva, R. F., Dtsch. Textiltech. (1972) 22 (3), 138.
47. Mecheels, J., Umbach, K. H., Melliand Textilber. Int., Eng. Ed. (1976) 5 (12), 1142.
48. Mecheels, J., Umbach, K. H., Melliand Textilber. Int., Eng. Ed. (1977) 6, (1), 76.
49. Mecheels, J., Melliand Textilber. Int., Eng. Ed. (1977) 6, (9), 841.
50. Mecheels, J. H., Umbach, K. H., "Clothing Comfort: Interaction of Thermal, Ventilation, Construction and Assessment Factors," Hollies, N. R. S., Goldman, R. F., Eds., Ann Arbor Science, Ann Arbor, Mich., 1977, p. 133.
51. Nesswetha, W., Melliand Textilber. Int. (1972) 53 (10), 1174.
52. Muller-Limmroth, W., Ehrenstein, W., Riebling, P., Nesswetha, W., Melliand Textilber. Int. (1973) 54 (9), 980.
53. Hollies, N. R. S., "Clothing Comfort: Interaction of Thermal, Ventilation, Construction and Assessment Factors," Hollies, N. R. S., Goldman, R. F., Eds., Ann Arbor Science, Ann Arbor, Mich., p. 107.
54. Fuzek, J. F., Ammons, R. L., ibid., p. 121.
55. Konda, A., Ohta, K., Toriumi, K., Misaizu, T., Sen'i Gakkaishi (1977) 33 (9), T453.

56. Kawabata, S., Akagi, Y., J. Text. Mach. Soc. Japan (1977) 30 (1), T13.
57. Yankelevich, V. I., Izv. Vyssh. Uchebn. Zaved. Tekhnol. Tekst. Prom-sti. (1971) 80 (1), 104.
58. Jaksic, D., Tekstil (1975) 24 (11), 815.
59. Kulikov, R. P., Kolotilov, V. G., Stebel'skii, M. V., Soboleva, L. M., Izv. Vyssh. Uchebn. Zaved. Tekhnol. Tekst. Prom-sti. (1977) 117 (3), 23.
60. Shivers, J. L., Yeh, K., Fourt, L., Spivak, S. M., "Clothing Comfort: Interaction of Thermal, Ventilation, Construction and Assessment Factors," Hollies, N. R. S., Goldman, R. F., Eds., Ann Arbor Science, Ann Arbor, Mich., p. 167.
61. Joki, M., Stverak, J., Textil (1970) 25 (4), 123.
62. Buzanov, G. B., Sukharev, M. I., Tekhol. Legk. Prom. (1973) 93 (3), 163.
63. Fischer, K., Fischer, E. O., Melliand Textilber. Int. (1975) 56 (3), 246.
64. Welfers, E., Textilveredlung (1971) 6 (3), 150.
65. Latham. B. J., Cloth. Res. J. (1973) 1 (2), 3.
66. Buzanov, G. B., Sukharev, M. I., Tekhol. Legk. Prom. (1973) 92 (2), 150.
67. Skaternikova, V. F., Izv. Vyssh. Uchebn. Zaved. Tekhnol. Tekst. Prom-sti. (1977) 119 (5), 28.
68. Rowlands, R. J., Text. Res. J. (1963) 33 (5), 343.
69. Spencer-Smith, J. L., Cloth. Res. J. (1976) 4 (4), 126.
70. Ibid., (1977) 5 (1), 3.
71. Ibid., (1977) 5 (3), 82.
72. Ibid., (1977) 5 (4), 116.
73. Cassie, A. D. B., J. Text. Inst. (1962) 53 (11), P739.
74. Fanger, P. O., ASHRAE Trans. Pt. II, (1967) 73.
75. Burton, D. R., ASHRAE J. (1972) 14 (8), 39.
76. Rohles, F. H., Jr., Nevins, R. G., Aerosp. Med. (July, 1973), 730.
77. Kjerulf-Jensen, P., Nishi, Y., Fanger, P. O., Gagge, A. P., ASHRAE J. (1975) 17 (1), 65.
78. Wyon, D. P., Fanger, P. O., Olesen, B. W., Pedersen, C. J. K., Ergonomics (1975) 18 (4), 359.
79. Text. World (1977) 127 (11), 69.
80. Rees, W. H., Shirley Link (Summer, 1969), p. 9.
81. "Advantages of Carpets and Rugs in Energy Conservation," The Carpet and Rug Institute, Dalton, Ga., June, 1977.
82. Verzbolauskas, L., Melliand Textilber. Int. (1978) 59 (1), 44.
83. Ozisik, N., Schutrum, L. F., ASHRAE Trans. (1960) 66, 228.
84. Pennington, C. W., Smith, W. A., Farber, E. A., Reed, J. C., ASHRAE J. (1964) 6 (2), 27.
85. Yellott, J. L., ASHRAE Trans. Pt. I, (1965) 71, 260.
86. Keys, M. W., ASHRAE J. (1967) 9 (10), 59.

87. Isfalt, E., "Use of Computers for Environmental Engineering Related to Buildings, "Kusuda, T., Ed., National Bureau of Standards Building Series 39, Washington, D. C., Oct. 1971, p. 477.
88. Petherbridge, P., "Third Shirley International Seminar: Textiles for Comfort," Shirley Institute, Manchester, 1971.
89. Dix, R. C., Lavan, Z., "Window Shades and Energy Conservation," Illinois Institute of Technology, Chicago, Ill., December, 1974.
90. Eccli, E., "Low-Cost, Energy Efficient Shelter for the Owner and Builder," Rodale Press, Emmaus, Pa., 1976.
91. Hastings, S. R., Crenshaw, R. W., "Window Design Strategies to Conserve Energy," National Bureau of Standards Building Science Series 104, Washington, D. C., June, 1977.
92. Text. Ind. (1978) 142 (1), 17.
93. Gunji, T., Nihira, K., Tsuboi, T., J. Text. Mach. Soc. Japan (1971) 24, T33.
94. Vera, G., Textilia (September, 1976) 52, 17.
95. Burberry, P., "Building for Energy Conservation," Architectural Press, London, 1978.
96. Givoni, B., "Man, Climate, and Architecture," Applied Science Publishers, London, 1976.
97. McIntyre, D. A., Build. Sci. (1974) 9, 247.
98. Benzinger, T. H., Mangum, B. W., Hill, J. E., ASHRAE Trans. Pt. II (1976) 82, 260.
99. Grot, R. A., Harrje, D. T., Johnston, L. C., Proc. Third Biennial Infrared Information Exchange, Warren, C., Ed., AGA Corp., St. Louis, Mo., August 24-25, 1976, p. 103.
100. Burch, D. M., Kusuda, T., Blum, D. G., 'An Infrared Technique for Heat-Loss Measurement," National Bureau of Standards Technical Note 933, Washington, D. C., April, 1977.
101. Tamura, G. T., ASHRAE Trans. Pt. I (1975) 81, 202.
102. Burch, D. M., Hunt, C. M., "Retrofitting an Existing Wood Frame Residence for Energy Conservation--an Experimental Study," National Bureau of Standards Report NBSIR 77-1274, National Bureau of Standards, Washington, D. C., July, 1977.
103. Speranskii, A. A., Kharitonov, V. M., Pakshver, A. B., Volokna Sint. Polim. (1970), 227.
104. Choy, C. L., Young, K., Polymer (1977) 18, 769.
105. Kato, D., Nakamura, T., J. Appl. Phys. (1976) 47 (10), 4528.
106. Volga, V. I., Frolov, V. I., Usov, V. K., Izv. Akad. Nauk SSSR, Neorg. Mater. (1973) 9 (4), 712.
107. Kalnin, I. L., Ram, M. J., Dix, R., "Exploratory Developments of Low Thrmal Conductivity Carbon Fibers, Part I," Wright-Patterson Air Force Materials Lab Report AFML-TR-72-151, Wright-Patterson AFB, Ohio, November, 1972.
108. Macnair, R., N., Arons, G. N., Coffin, L. G., Text. Res. J. (1977) 47 (5), 324.
109. Thibodeaux, D. P., Baril, A., Jr., Int. Dyer, Text. Printer, Bleacher Finish. (1974) 151, 35.

110. Sakalauska, A., Zdanavicius, I., Monkeviciute, G., Paskevicius, V., Girlevicius, A., Visokinskas, A., Nauchno-Issled. Tr. Litov. Nauchno-Issled. Inst. Prom-sti. (1972) 2, 135.
111. Hansen, R. H., J. P. Stevens & Co., Inc., U. S. Patent 3,607,591 (1971).
112. Clark, R. P., Cloth. Res. J. (1974) 2 (2), 55.
113. Roben, K., Melliand Textilber. Int., Eng. Ed. (1973) 2 (4), 315.
114. Beckstein, H., Textilveredlung (1974) 9 (9), 401.
115. Wegener, W., Coll-Tortosa, L., Lenzinger Ber. (1976) 41 (8), 5.

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In Energy Conservation in Textile and Polymer Processing; Vigo, T., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 1979.

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ACS Symposium Series; American Chemical Society: Washington, DC, 1979.