Textiles and the Chemical Industry: A Marriage

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ABSTRACT
At its national technical conference last month in Atlantic City, AATCC presented its Olney Medal for technical and scientific achievement to Herman B. Goldstein, vice-president of planning for the chemical division of Sun Chemical Corp.

Following acceptance of the medal and the $1,000 honorarium which accompanies it, Goldstein presented the traditional medalist's address. In it he traces many of the outstanding inventions and developments of the past 100 years that have been mutually beneficial to both the textile and the chemical industries. Current approaches to some of the problems faced by both industries today are also discussed.

KEY TERMS
Durable Press
Dust Control
Employee Health
Pollution
Solvent Preprinting
Wastewater Treatment

IN considering possible topics for presentation on this occasion, the supportive role of the chemical industry for the textile industry kept re-asserting itself as the dominant theme. From the very early days when weaving and knitting of textiles were moving out of the kitchen and were becoming large scale industrial processes, the chemical industry was supplying sizes and lubricants to make the mechanical processes efficient, and dyes and finishes to make the resultant fabrics attractive. In effect, we've had a happy marriage between the textile and chemical industries, and although it's difficult to perceive which is the bride and which is the groom, the overall effect has been mutually beneficial, as in any successful marriage.

Let us then look at some of the developments which have worked for the betterment of the textile industry, and see how the chemical industry participated in them.

Table I—Outstanding Developments

<table>
<thead>
<tr>
<th>Invention</th>
<th>Reference</th>
<th>Inventor</th>
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<tbody>
<tr>
<td>Synthetic Spun Fiber</td>
<td>(1)</td>
<td>Count Hilaire de Chardonnet</td>
</tr>
<tr>
<td>Synthetic Surfactants</td>
<td>(2)</td>
<td>Gunther (I. G. Farbenindustrie)</td>
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<tr>
<td>Disperse Dyes</td>
<td>(3)</td>
<td>Baddiley et al. (British Dyestuffs Corp.)</td>
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<tr>
<td>Compressive Shrinking</td>
<td>(4)</td>
<td>Cluett (Cluett Peabody)</td>
</tr>
<tr>
<td>Nylon Fiber</td>
<td>(5)</td>
<td>Carothers (duPont)</td>
</tr>
<tr>
<td>Chloromethylated Quaternaries</td>
<td>(6)</td>
<td>Rogers (I.C.I.)</td>
</tr>
<tr>
<td>Polyester Fiber</td>
<td>(7)</td>
<td>Winfield et al. (Calico Printers)</td>
</tr>
<tr>
<td>False Twist Texturizing</td>
<td>(8)</td>
<td>Heberlein et al. (Heberlein)</td>
</tr>
<tr>
<td>Reactive Dyes</td>
<td>(9)</td>
<td>Rattee et al. (I.C.I.)</td>
</tr>
<tr>
<td>Perfluorinated Compounds and Polymers</td>
<td>(10)</td>
<td>Sherman et al. (3M)</td>
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<tr>
<td>Soil Release</td>
<td>(11)</td>
<td>Marco (Deering Milliken)</td>
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History
In the early days, finishes were predominantly of a nondurable nature, such as soaps, sulfated oils, starch and talc. Such finishes were designed to improve the esthetics and apparent quality of the fabric at point of sale, but usually their effects were lost entirely after the first laundering. Finishes of these types are still used to some extent on low-end goods, but it is obvious that such finishes are not likely to engender consumer loyalty.

With increasing consumer sophistication, the textile industry organized itself to provide fabrics with improved functional and esthetic effects which would persist even after many washings or drycleanings. A chronology limited to the last century of some of the most noteworthy developments is given in Table I. For purposes of brevity, those innovations which have had a long lasting effect and are of commercial significance have been in-
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exceptions conceived within the textile industry itself. Ultimately, of course, in those latter cases, it fell upon the shoulders of the chemical industry to supply the chemicals needed to put those processes into practice efficiently and economically.

It is readily apparent from examination of Table I that one important group of developments has been omitted. This is the group (Table II) comprising resins and crosslinkers. These developments and their impact on the textile industry merit comment.

First of all, the pioneering discovery of Foulds, Marsh and Wood, while they were employed at Tootal Broadhurst Lee (12, 13), deserves special mention because, after all, their work is the cornerstone on which all subsequent resin developments rest. To be sure, Foulds and his colleagues incorrectly assumed that the beneficial effects they obtained resulted from the formation of a resilient resin core within the voids of the fiber. They did not recognize the fundamental role of crosslinking; moreover, they strongly objected (18) to this concept long after it had been proposed by others (19, 20). The confusion resulting from the controversy between the two camps, one advocating resin formation and the other backing the crosslinking theory, tended to inhibit the logical development of these processes for some years. However, this is now past, and we want to take this opportunity gratefully to acknowledge our indebtedness to Foulds, Marsh and Wood.

Although theoretically applicable to all types of cellulose, in point of fact the innovation of Foulds and his colleagues was limited to the treatment of rayon. Resin treatments of cotton languished until Burton launched a worldwide promotional program for Everglaze (14). In this process, cotton is impregnated with urea-formaldehyde resin precursors, and then dried at low temperature to prevent premature polymerization of the resin. The treated fabric is then subjected to some mechanical deformation on a heated calender such as glazing, embossing or schreinering. Following the calendering, the fabric is heated to cure the resin fully. The mechanical effects obtained in this way are durable to laundering; as such, Everglaze became a resounding success throughout the world. At the same time, it opened our eyes to the opportunities and problems associated with resin treatments of cotton.

The next milestone is the commercial development of the dimethylol cyclic (DMHU) process at Rohm and Haas. Although this compound or intermediates had previously been known in both the scientific (21) and patent literature (22), it was Gagliardi, Hurwitz and Nuesse at Rohm and Haas who first recognized the enormous advantages of using this difunctional cyclic crosslinker (15). In the first place, because the nitrogen atoms were completely substituted and free of hydrogens, we had, for the first time a moderately chlorine-resistant finish suitable for white cottons, which could be laundered with minimal treatment with chlorine bleach. Secondly, because DMEU does not form hard insoluble resins, it tends to give a much softer hand. A peripheral advantage of this non-resin-forming property was that DMEU could be used with excellent results in Bancroft’s Everglaze processes (23) because there was little or no tendency for DMEU to build up and elong the engraving in the calender rolls, unlike other finishes available at that time. Finally, it was found that DMEU could be cured readily with a wide variety of catalysts to give finished effects which were much more durable to home laundering.

As you may have noted, I have qualified the durability of DMEU and limited its usefulness to home laundering. This is due to the fact that, although DMEU has excellent hydrolytic resistance under the alkaline environment present during the washing step, it has exceedingly poor hydrolytic resistance under acidic conditions. Thus DMEU was found unsuitable as a resin finish on any fabrics which were destined to be sent to commercial laundries because of their regular use of acid, sour in their final rinse. The deterioration of DMEU finish as a result of exposure to acid sour manifests itself first in the loss of chlorine resistance. Thus, in practice, DMEU had distinct limitations for treatment of cottons, particularly those fabrics which were likely to be sent to commercial laundries and bleached repeatedly.

This shortcoming in DMEU was the driving force in Sun’s development program to produce a finish for cotton which would retain its chlorine resistance regardless of the method of laundering.

This work, under the direction of Don Gagliardi, ultimately resulted in the Sun family of triazone-based crosslinkers. Here again, although the basic chemicals had been known earlier (24, 25), it was not until Gagliardi discovered the important advantages of

<table>
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<th>Invention</th>
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<th>Year Introduced</th>
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<tbody>
<tr>
<td>Anticrease</td>
<td>(12, 13)</td>
<td>Foulds et al.</td>
<td>1928</td>
</tr>
<tr>
<td>Durable Glazing</td>
<td>(14)</td>
<td>Bener (Bancroft)</td>
<td>1938</td>
</tr>
<tr>
<td>Dimethylol</td>
<td>(15)</td>
<td>Gagliardi et al. (Rohm &amp; Haas)</td>
<td>1948</td>
</tr>
<tr>
<td>Cyanoethylurea</td>
<td>(16)</td>
<td>Gagliardi (Sun Chemical)</td>
<td>1952</td>
</tr>
<tr>
<td>Dimethylol a-Triazones</td>
<td>(17)</td>
<td>Goldstein (Sun Chemical)</td>
<td>1963</td>
</tr>
<tr>
<td>Postcured Permanent Press</td>
<td>(17)</td>
<td>Goldstein (Sun Chemical)</td>
<td>1963</td>
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Fig. 1. Shape retention after crosslinking.
triazones that such products were introduced commercially for unrestricted treatments of all types of cottons, both colored and white, which could be laundered and bleached in any way desired.

As you may have anticipated, the other development on which I'd like to elaborate pertains to permanent press, in particular, postcured permanent press (17).

As most of you recall, the development of the older wash and wear process was both a blessing and a problem for the cotton apparel industry. The basic phenomenon involved here (Fig. 1) is that a treated fiber, yarn, or fabric tries to return to the same geometric orientation it was in at the moment crosslinking occurred.

Thus, a cotton fabric given a typical antical for wash and wear treatment was impregnated with a crosslinker and then dried and cured in the piece. At the time of curing, the fabric was stretched taut and was in a smooth, flat condition. When garments made from this fabric were worn or laundered, all wrinkles and puckers tended to disappear and the fabric dried smooth. To that extent, the wash-wear treatment was a blessing to the housewife.

Unfortunately, when this same wash-wear fabric was cut into garments in which styling required deliberate creases or pleats, such garments lost much of their appeal, because as soon as they were washed, all desired creases and pleats disappeared along with the unwanted wrinkles. In addition, for various reasons (26), a wash-wear treatment impregnated with a crosslinker was tended to disappear and the fabric dried smooth. To that extent, the wash-wear treatment was a blessing to the housewife.

As can be seen, the critical factor in postcuring is to defer the curing, and therefore the crosslinking, until the garment has been sewn and pressed. This, as we have already discussed, provides garment shape retention with excellent seam smoothness. We don't have time to wend our way through the early development program of this postcure process, but I would like to relate a little scenario that had an enormous impact on the course and pace of our activity.

As a postscript to this story, however, I'd like to point out that this process, which was stimulated by varied cotton interests, actually turned out, instead, to be an enormous stimulus in the sale of synthetics, particularly polyester fiber. Figure 3 charts
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the total annual production figures for polyester fiber in the USA (35). Please note that 1964 was the first full year in which the post-processed permanent press process was available, and the trend to the use of polyester as a reinforcing fiber was in full swing. I believe that the change in slope of the production curve which occurred in 1964 was more than a mere coincidence. I’m sure that these figures are a source of great satisfaction to some people just as they must be a source of frustration to others.

As another example of the peripheral impact of the permanent press processes, Figure 4 shows annual shipments of household tumble dryers and percent saturation (36).

The plateau in shipments which occurred in the years 1955 to 1963 was apparently caused by the uncertainties regarding the merits of the earlier wash-wear treatments, but represented a long base from which the accelerated growth occurred from 1965 onward as a result of permanent press. The rate of increase of saturation since 1965 is equally striking.

Future

If we study the developments listed in Tables I and II more closely and look behind the scene, so to speak, we see that the chemical industry has made another “contribution” to the textile industry. This, in effect, is the contribution we have made to the pollution problems of the textile industry. It is readily apparent that most of the pollutants with which the textile industry is concerned, result from chemicals, dyes or other materials which are added during the manufacture and processing of the cloth (37). After they have served their purpose, it is necessary to remove residues of such agents, and this frequently results in environmental problems with pollution of streams and atmosphere. During use or removal, such materials may also have an adverse effect on the health and safety of the employees, or possibly on the wearers of the treated cloth. With the onset of new Federal and State regulations governing such factors, and with such regulations growing stricter day by day, these problems of pollution and safety take on enormous proportions for the future. The solutions to such problems, or lack of same, will undoubtedly represent the difference between success and failure for many textile mills.

Because of the critical importance of such problems, I feel it is appropriate for me to devote the balance of this address to our views concerning some of them and what we can do about them.

As a basis for our consideration, let’s first review briefly the current situation and the most likely future prospects for the regulations promulgated by the Environmental Protection Agency (EPA) and the Office of Safety & Health Administration (OSHA).

First of all, the EPA mandate is to reduce and then eventually to eliminate pollution of our waterways, our atmosphere, and our land areas (both surface and subsurface). For example, with regard to stream pollution, by 1977 it will be required that all companies discharge all their effluents in such a manner that the water in their sewers will not be polluted beyond the “best practicable treatment.” By definition, the best practicable treatment means a level of treatment which can be achieved by most companies in the industrial segment, at a cost not so high as to force those companies out of business.

Going further, it is the present intent of Congress that, by 1983, all companies will use “best available technology” to clean up their effluent streams. This means that if anyone is doing it anywhere, you can be asked to do it. And finally, by 1985, all aqueous effluent will be required to show zero pollutant content.

To date, in general, EPA and the individual states have placed greater emphasis on control of pollution of the waterways than the other aspects of industrial atmospheric and land pollution. But we can fully expect them to intensify those programs as well. For example, we can already see strong pressure from some states to greatly reduce the exhausting into the atmosphere of certain types of chemicals (38). And this trend will certainly accelerate (39).

On the same philosophical basis, OSHA is moving ahead to make our working places safer for all employees. This includes not only the physical facilities, also precautions to prevent workers from handling or being exposed to irritating, toxic or carcinogenic materials (40).

Thus, it is readily apparent that the discharge of most chemicals into the environment will, at the very least, be significantly restricted and, in many cases, completely forbidden. At the same time there will be even-tightening restrictions regarding the exposure of workers to hazardous or toxic substances.

With that thought in mind, let’s look at some of the trouble spots in various stages of textile production.

Sizing

In the rush to reduce the biochemical oxygen demand (BOD) of desizing liquors, many greige mills replaced part or all of the starch in their warp size with carboxymethyl cellulose (CMC) or polyvinyl alcohol (PVA). These substances do, indeed, have much lower BOD, but that is simply due to the fact that they do not readily decompose when subjected to conventional biological effluent treating processes. Thus, unless special precautions are taken, a high percentage of the influent CMC and PVA pass right through the sewage treating plant, and enter the waterway as such. Obviously, this will be forbidden in the foreseeable future. In considering how to overcome this problem, one approach would be to go back to good old starch which can be decomposed adequately by conventional activated sludge treatments. However, because of the enormous BOD content of typical starch desize liquors, many mills would find it necessary to install greatly increased sewage treating facilities. Another ap-

Fig. 4. Shipments of tumble dryers and saturation.
proach would be to take advantage of the recently recognized phenomenon of bacterial acclimatization (41). By such procedures, it is possible to develop bacterial strains which have more efficient PVA digesting power. Through use of a couple of such acclimatized activated sludge systems in series, it seems that PVA content in the effluent could be reduced close to zero.

On the other hand, I think a more logical course to take would be to use a solvent size and desize process. This completely eliminates the problems of aqueous effluent, and even offers the potential advantage of partially recycling the size. But it should be emphasized that, in the long run, the use of solvent-size-desize processes, or any other large scale textile solvent process, will not be ecologically sound until more efficient methods of solvent recovery have been developed. As I've pointed out in an earlier paper (42), unless we have substantially more efficient solvent recovery systems, we shall simply be exchanging a stream pollution problem for an atmospheric pollution problem.

Dyeing

The dyeing process has always been a source of heavy pollution primarily because of the color rinsed off. The introduction of carrier dyeing of synthetic fibers has intensified the problems and is the cause of much concern based on newly established EPA and OSHA standards for many of the chemicals which are widely used as carriers. The increased use of higher pressure dyeing equipment in the last 3-6 years has helped appreciably because the higher pressures permit use of much lower concentrations of carriers. Even so, the active ingredients commonly used as carriers frequently have objectionably high levels of toxicity or have very obnoxious odors. Obviously, there is intense research activity to provide carriers of improved ecological properties. There is much further room for improvement, but the first encouraging step in this direction was in the introduction of perchloroethylene based carriers.

The basic reasons for our enthusiasm about "perc" (perchloroethylene) are: (1) 100% of the perchloroethylene present in the dyebath is absorbed by the fabric during dyeing, and thus the spent dye liquor does not represent a stream pollution problem because there is no perc in it; (2) when the dyed fabric is dried, the perc is driven off the goods and goes up the stack. And of course, perc is one of the solvents approved under California's Rule 66 as well as North Carolina's recently issued rules, so it should not result in atmospheric pollution (39).

To be sure, the simple use of perchloroethylene as a carrier leaves much to be desired. For examples, some commercial perc-type carriers may be deficient for one or more of the following: spotting due to poor emulsion stability; streakiness due to poor leveling; excessive chafing and crack marks; excessive trimer deposits; poor barre coverage. This seems like a formidable list of objections, but I'm happy to be able to report that it has been possible to eliminate essentially all of these problems while preserving perc's excellent ecological properties.

Printing

Printing pastes, in general, and solvent emulsion type pastes in particular, are the source of enormous amounts of pollutants (43). First of all, color shop wastes contribute both very high color and BOD. Secondly, during drying of the prints, tremendous amounts of solvent are evaporated and vented to the atmosphere.

There are a few possible approaches to solve this problem in whole or in part. Among them is use of straight aqueous dispersions with water-soluble or dispersible thickeners and binders. This of course, eliminates the problems associated with the solvents, but does nothing to eliminate the BOD from the thickeners and binders.

Another possible approach is the use of completely solvent-free systems such as with our Suncure ultraviolet-activated binders. Although we are just at the front edge of the research thrust on this approach, it looks very encouraging to provide almost instant fixation through ultraviolet radiation, without the need for heating to evaporate either solvent or water.

Aside from the obvious ecological advantages which will result from the use of completely solvent-free systems, the extremely rapid fixation which is possible with ultraviolet curing offers advantages which will result from the use of completely solvent-free systems, the extremely rapid fixation which is possible with ultraviolet curing offers the possibilities of much more rapid process-
note that Product C provides sensitized goods which meet the requirement of Levi-Strauss which went into effect in March 1972 and Product D meets the Levi-Strauss requirements which are slated to go into effect this year.

Figure 6 shows some very interesting data which is based on our own laboratory work, and largely confirmed by work done in their cutting rooms. Here we see the correlation between the free formaldehyde in fabric with the formaldehyde content in the air in the cutting room. Obviously, the relationship between the free formaldehyde on the fabric and the formaldehyde content in the air will vary to some extent with certain physical aspects of a given cutting room; for example the ratio of amount of cloth in the room to the cubic feet of air in the room, the amount of air circulation and the amount of fresh air introduced per unit of time, and so forth. But even so, the data in Figure 6 are very informative in that they show it is necessary to drop to approximately 1000 ppm or less of free formaldehyde on the cloth to reduce the free formaldehyde in the air to less than 3 ppm which is now required by OSHA for 8-hour exposure.

Inspection

The last steps in a textile dying and finishing plant are inspection and put-up. Since the advent of resin finishing of cellulose and cellulose blends, and especially permanent finishing plant are inspection and held to it.

Conclusion

We have reviewed a number of important areas where the marriage of the textile and chemical industries has produced offspring of enormous importance to the consuming public throughout the world. We have also touched on several important aspects where we are now actively working to ameliorate textile industry problems related to environmental protection and worker safety.

In this connection, I should stress that we have taken the position that such problems must be solved without introducing new problems or sacrificing performance.

With this kind of attitude we should be able to expect many more years of conjugal bliss for both the textile and chemical industries.

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