To the chemist, light is something more than just the absence of darkness. It is a form of energy that can change the physical and chemical nature of substances.

Light consists of a group of electromagnetic radiations capable of stimulating the eye. It is a small portion of a wide range of radiations that include radio and radar waves, diathermy waves, ultraviolet rays, and X-rays.

When the radiations are arranged in a progressive order of their wavelengths, the array is referred to as a spectrum. The visible spectrum begins at the long-wavelength end with red and passes through the rainbow colors to violet at the short-wavelength end, each color having a progressively shorter wavelength. When all of the visible wavelengths stimulate the eye at once, the effect is perceived as white light. We use the word light to include also invisible radiations immediately adjoining the visible spectrum, the infrared at one end and the ultraviolet at the other.

Radiation absorbed by substances increases the energy content of their molecules and so may cause changes, the nature of which depends upon the kind of radiation absorbed. Thus, long-wavelength radiation, when absorbed, increases the average speed of molecular movements and so raises the temperature of the absorbing material. Short-wavelength radiation may cause displacement of electrons in the atoms composing each molecule of the absorbing substance and activate it so that it becomes chemically unstable. A chemical change resulting from this absorption of radiation is known as a photochemical reaction.

Various workers who have studied the photochemical reaction of cotton have shown that the most important effect of light is an activation of the cotton cellulose. It accelerates enormously the reaction of cotton cellulose with oxygen of the atmosphere.

We do not know when the discovery was made that light has a harmful effect on cotton textiles. About the middle of the nineteenth century, manufacturers of curtain and casement cloth noticed that the materials lost more strength in the parts directly exposed to light than in the shaded folds. Probably the systematic investigation of photochemical action on cotton was fostered in the latter part of that century by Georges Witz, vice president of the Société Industrielle de Rouen, who published results of some original studies on oxidized cellulose. That in itself would be of academic interest only, were the oxidation of cellulose not accompanied by changes in the strength and appearance of the cotton. Because of the importance of such characteristics to the users of cotton textiles, it is of practical interest. During the First World War the harmful effect of light on textiles became a military problem. The Second World War stimulated further research on the mechanism of deterioration and the development of protective treatments.

Many scientists now are engaged in research to evaluate and solve the problem of photochemical degradation of cotton. Basic to this research is an understanding of the chemical nature
of cellulose, of which cotton is almost entirely composed.

Cellulose is a polymer substance: Its chemical structure consists of a simple molecular pattern that is repeated many times. The patterns are joined like links of a chain into long, threadlike molecules. The chainlike structure gives cotton its fibrous qualities. Light attacks the cellulose at the points of linkage and thus shortens the average chain length. Although photochemical degradation, until it is well advanced, does not alter the feel or appearance of the cellulose, it reduces the strength and finally causes the loss of all fibrous properties.

To approach logically a study of the destruction of cotton by light, one has to know something of the quality and quantity of the light.

Because the quality of light depends on wavelength, an evaluation of the effect on cotton samples requires selection and control of the wavelengths. That is accomplished in several ways: (1) By selecting a light source that radiates its energy in narrow bands of wavelengths, as does the mercury arc; (2) by using conjunctively a wavelength selector, such as a spectrometer, and a light source that radiates all wavelengths of the light spectrum (known as a continuous source); (3) by using a continuous source and shutting out all but the desired portion of the spectrum with colored-glass filtering screens.

None of the methods is perfect. In the first, the kind of light available is limited to the particular wavelengths characteristic of the source. The second gives the greatest selection and purity of radiation, but it is limited because of the very small area illuminated by the selected radiation and because of the feebleness of the beam obtained with even the most powerful sources. The third is limited by the nature of glass color filters, which either transmit efficiently broad and often overlapping spectral bands or transmit inefficiently the required narrow and exclusive spectral bands.

The amount of light falling on the cotton can be measured accurately by several devices. Bolometers, thermopiles, pyrheliometers, and radiometers operate on the principle of the conversion into heat of all radiation falling on an especially prepared surface. The resulting thermal effects can be measured accurately by a change in electric current or potential, the expansion of mercury in a glass tube, or the increase in velocity or torsion of a suspended, rotating vane. Actinometers depend on measuring the chemical change in a system that reacts in proportion to the total amount of light it receives. Photocells of various kinds either generate or conduct an electric current proportional to the amount of light falling upon the sensitive surface.

After one has subjected samples of cotton to the action of known quantities of light of selected quality, he can measure the photochemical effects by several means. The most direct method, but not the most sensitive, is to compare the tensile strength of the cotton before and after exposure, as determined by a machine that registers the force necessary to break the material by pulling. Because of the inherent variability of the mechanical properties of cotton, even the most carefully determined strength measurements cannot be precisely duplicated. Because of its directness, speed, and simplicity, however, the breaking-strength method is widely used.

A more sensitive index of photochemical damage is in the measurement of the viscosity of a solution of the exposed cotton. Cuprammonium hydroxide solution, a solvent made from ammonia, water, and copper, will convert cotton into a clear solution. Solutions thus made with undegraded cotton are thick, viscous liquids, because the long, threadlike molecules of cellulose move with difficulty past one another when the liquid flows. Badly degraded cotton, whose chainlike molecules are broken and fragmented by photochemical reaction, however, produces a thin, watery solution.
Cotton in various stages of degradation yields solutions with all gradations of viscosity between that of cotton with a high degree of polymerization and that of seriously damaged cotton with a low degree of polymerization. For example, data obtained by exposing cotton to the action of sunlight for progressive periods up to 3 months gave viscosity indices of 0.07, 0.04, and 0.03 poise (unexposed control, 0.37 poise), which indicates an average molecular chain length in each instance of 1000, 600, and 430 polymer units (unexposed control, 2250). By way of comparison, the results were approximated by 30 hours of exposure to radiation from either the carbon-arc or mercury-arc lamp, two sources of artificial light.

Other measures of the photochemical damage to cotton by exposure to light depend on detecting and following the chemical changes produced by irradiation. One of these, the copper-number method, measures the ability of the cotton to reduce the copper in a copper salt solution from the high- to the low-valence form. The reducing power of the cotton cellulose depends on the reaction of the terminal group of atoms at the end of each chainlike cellulose molecule. It is obviously greater when many short-chain molecules, rather than few long-chain molecules, compose a given sample.

Another method of following the chemical change produced in cotton by radiation is the methylene-blue test, which depends on the affinity of the basic dyestuff methylene blue for oxidized cellulose, the cotton absorbing more of the dye as the oxidation proceeds.

Still another method requires a closed system, so that analyses can be made of the sample and its surrounding atmosphere before and after irradiation to detect evidence of oxidative reaction.

These methods, developed by many investigators, have contributed to a growing body of information on the problem of the deterioration.

According to the accepted theory of photochemistry that higher energies are associated with the shorter wavelengths of light, the ultraviolet light should be expected to be the most damaging to cotton. That has been shown by the rapid degradation of cellulose exposed to light rich in ultraviolet, such as the light from mercury- and carbon-arc lamps. Although the proportionately greater effect of ultraviolet light made it customary to disregard the effects of other parts of the spectrum, it was our thought that light from other parts of the spectrum might not be insignificant. This prompted us to investigate the spectral distribution of the cotton-degrading radiation in sunlight.

For the investigations, we used a special cabinet in which samples of cotton fabric were exposed to sunlight and protected from rain, wind, and dust. The samples were arranged so that each was irradiated solely with the sunlight transmitted by one of six glass color filters, which divided the light spectrum into five sections, the sixth being transparent equally to all wavelengths. Special automatic devices recorded the cumulative quantities of solar energy received by each sample beneath its respective filter. Sample temperatures were kept nearly constant by the circulation of water of controlled temperature through broad-surfaced metal cells on which the samples were mounted. The cabinet used solar radiation with maximum efficiency by turning automatically to follow the course of the sun. During the 8 months of the exposure, portions of the samples were withdrawn periodically.

Although the ultraviolet portion of the sunlight demonstrated the highest degrading efficiency, the damaging influence of sunlight was not limited to the shorter wavelengths of light. Even at a lower degrading efficiency, energy of longer wavelength than ultraviolet light was definitely effective. This was noticeable probably by reason of its greater abundance in sunlight, which,
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When it reaches the earth's surface, has less than 3 percent of ultraviolet. It may be that the effectiveness of the ultraviolet light is further reduced by an antagonistic action of longer wavelengths. Scattered evidence reported by various workers supports the view that the presence of longer wavelengths of light mixed with the ultraviolet light lessens the photochemical effectiveness. Evidence of this nature was obtained in experiments in which samples exposed under a blue filter suffered more degradation than others exposed under a clear filter and more than some samples which were exposed with no filter at all.

The relative effectiveness of light from various parts of the spectrum probably depends more upon the amount of light absorbed than upon the differences in its energy content. It is well known that certain dyestuffs make cellulose more sensitive to light. In a study of the increased degrading effect of light caused by dyes, Dr. Gerard S. Egerton, of the College of Technology, Manchester, England, offers an explanation of the oxidative reactions to which the photochemical degradation of cotton cellulose is due. He states that undyed cotton is photochemically activated by absorption of light energy in the ultraviolet section but that cotton dyed with certain "active" dyes is activated by energy which the dye absorbs from the visible region of the spectrum. The actual oxidation is accomplished by a volatile oxidizing agent, probably hydrogen peroxide, formed at the cellulose surface. In substantiation of this idea is offered the evidence from an experiment in which a set of alternate dyed and undyed yarns, strung closely together but not touching, was exposed in a small enclosed chamber. The undyed yarns were definitely more degraded when exposed near the dyed yarns than when exposed away from them. In all instances, the presence of both oxygen and moisture was necessary to produce degradation.

The results seem to reduce to relatively simple terms the action of light upon cotton—but the problem is probably more complex. At the Institute of Paper Chemistry, in Appleton, Wis., Robert A. Stillings and Robert J. Van Nostrand found evidence that radiation alters or activates cellulose in some way, even in the absence of oxygen and water vapor, so that the cellulose can be oxidized subsequently by the atmosphere in the absence of radiation.

Textiles are rarely exposed to light isolated from other factors of deterioration. Light is usually a part of weather, and light-protective treatments of textiles must be directed also against rain, micro-organisms, and atmospheric contaminants.

Finishes that afford cotton materials protection from the weather have long been known, but they are usually waxy, tarry, and sticky, and rob the fabric of practically all textile properties. Research continues for a finish closer to the ideal, which would seal the fibers against moisture, screen the fabric from the deleterious action of light, and inhibit biological growths, without being injurious to the user. Furthermore, we need a protective finish that would be permanent, with no adverse or objectionable effect upon the weight, strength, appearance, body, and hand of the fabric. It should also be simple and inexpensive to apply.

One approach to the ideal treatment has been the attempt to modify chemically the molecular structure of the cellulose and still retain the textile qualities of the original fibers. Such chemical modification is generally effected by adding on groups of atoms at the reactive points that characterize each link of the cellulose chain. The new groups occupy or block those reactive points and render them inactive. One such modification is had by partial acetylation, a treatment long known in theory but just recently developed along practical lines by the Department of Agriculture. Cotton treated by the process, which does not distinguishably alter the appearance or feel of the
material, has been successful for a number of uses in which unmodified cotton has failed.

The increasing development of plastics or synthetic resins offers many possibilities for their use in protective treatments for textiles. In many places, experiments are in progress on the utilization of resins for fabric finishes. We have tried urea and melamine formaldehyde resins as experimental protective finishes. Textile qualities have not been impaired seriously, and fabrics treated with some of the finishes have resisted sunlight and weather for a year without loss of strength, although untreated material exposed similarly lost half its original strength.

It is easy to see that progress in research on these finishes is delayed by the necessity of subjecting all experimental treatments to protracted outdoor service tests for sometimes as much as a year. Rapid exposure methods that we could carry on in the laboratory would be a great help.

Many attempts have been made to develop such faster methods. For testing the protective treatments of cotton cloth, use has been made of the susceptibility of cellulose to the very short wavelength ultraviolet radiations produced by the carbon-arc lamp. In fact, a treated fabric that would require a year of exposure to natural sunlight in order to show a strength loss of but 15 or 20 percent could be broken down completely in a week by radiation from that source. The results obtained by such artificially accelerated means will be of little practical value unless they duplicate with reasonable accuracy the results of exposure to natural sunlight.

An illustration is found in the results that we obtained from a series of 20 experimental finishes on cotton duck exposed to sunlight and weather for a year. We subjected identically finished samples to an accelerated laboratory test that made use of light from a carbon-arc lamp. In each instance, the protective finish was evaluated as poor, good, or excellent on the results of the test. Fourteen out of twenty of the finishes were rated the same by both exposure methods—a degree of correlation of 70 percent between the natural and the laboratory tests. The results do not justify complete reliance on accelerated methods to screen good treatments from poor, but they show promise that the method may develop into a reliable timesaver.

P. James Fynn, a graduate of Tulane University, has been engaged since 1944 in work on the accelerated aging of cotton textiles and on finishes for protecting cotton textiles from the action of light and weather. In 1949 he joined J. C. Penney Co., Inc., where he is assistant to the director of research and testing laboratories.

James D. Dean, after graduation from Brown University, was employed as a chemist in a New England cotton-finishing plant. He remained in the industry more than 20 years, serving with several companies as chemist, purchasing agent, and plant superintendent. In 1942 he joined the Southern Regional Research Laboratory, where he heads the cotton chemical processing division.

A pound of cotton has about 90 million fibers. A bale of cotton has a gross weight of about 500 pounds. Some cottons grow on small trees. The entire cotton fiber is a single tubelike cell. No other vegetable fiber has the spiralike form of cotton fiber. The natural colors of cotton are brown, green, cream, and white. The length of the cotton fiber may be from 1,000 to 3,000 times its diameter. The tensile strength of cotton approximates the tensile strength of steel. Cotton is produced on six continents. The cotton fiber is the most-used vegetable textile fiber.—James N. Grant, Southern Regional Research Laboratory.