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The Deteriorating Effect of Light on Museum Objects:

Principles of Photochemistry, The Effect on Varnishes and Paint Vehicles and on Paper

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Among the agencies that are able to hasten the deterioration of materials in museums, such as heat, moisture, dirt, and the reactive gases in the atmosphere, comparatively little attention has been given to the action of the radiant energy of natural and artificial sources of illumination. One of the earliest investigations of this specific problem appeared in 1888 (41). A number of studies of the fading of water colors followed in the next several decades. The *Manual on the Conservation of Paintings,* published by the International Museums Office in 1940, does not specifically mention these studies, although it devotes about 80 lines to the action of light on paintings. Plenderleith, in his authoritative book of 1956, devotes about the same number of lines to the action of light on textiles (38).

Beginning in 1952, however, with the report of Professor Genard on the ultraviolet radiation emitted by tubular fluorescent lamps (19), an increasing number of publications has appeared concerning the effect of light on museum objects. There are several reasons for this. First, the possibility of using modern fluorescent lamps has offered a number of attractions to muse-

ums: lower power consumption, the tubular form of the lamps, low heat, and a variety of colors. Consideration of these lamps naturally raised questions concerning the characteristics of the ultraviolet energy that they emit. Second, the public has become accustomed to higher levels of illumination at the same time that architects have found large expanses of window glass to be an attractive feature. Thus, the question of the intensity of illumination in museums needs to be considered anew. Third, a number of chemical compounds are currently being marketed for use in protective coatings and plastic sheets to remove ultraviolet radiation. The possibility of using such protective materials has raised again the question of the significance of ultraviolet radiation in deterioration. A fourth and often overlooked reason is that the proper tools with which to study these problems—spectrophotometers, light-intensity meters, filters, etc.—have become available to the average investigator in recent years.

To get answers to some of the questions currently being raised, one may first search the technical literature to learn what is already known concerning the action of light

on particular materials. Research can then be planned to fill the major gaps in our knowledge. With such a plan in mind, the National Gallery of Art Research Project at Mellon Institute instituted a long-term program to study the effects of light on museum objects. Some aspects of the research have been going on for as long as eight years. One of the first steps in this research program has recently been completed: a review of the characteristics of radiant energy and the general factors that control damage by light (16). In this review, reference is made to the many publications that have appeared in the last decade concerning the problem of photochemical damage in museums.

Along with the preparation of this review, there has also been a search of pertinent technical publications. A glance at *The Chemical Action of Ultraviolet Rays* (Ellis and Wells) and more recent surveys, will quickly reveal that there is an extensive literature concerning the action of light on textiles, paints, varnishes, and plastics (10)(40)(42). It may be surprising to some, however, to find how few of the results of this considerable research can be

applied directly to answer the questions that arise in a museum. One reason for this is that few of the studies have been carried out under carefully controlled conditions of temperature, humidity, and illumination. As a consequence, only a limited number of the results can be interpreted in terms of museum exposure. In addition, few of the materials studied have been the traditional fabrics, paints, dyes, and pigments of historic interest.

The first part of the survey of the literature is presented herewith: a section concerning the effect of light on varnishes and paint vehicles and one concerning the effect on paper. In addition, the remarks appropriately begin with a review of the principles of photochemistry. A future publication will summarize the effect of light on textiles, pigments, and dyes.

With the preparation of these summaries, the review of principles and the preliminary survey of the literature are completed. Results of new research on the effect of light on varnishes have already been published, and it is hoped shortly to complete several studies on fading. The investigation of additional photochemical problems will be undertaken in the future.

Principles of Photochemistry

Photochemistry is a rather specialized subject. Yet, an appreciation of a few of the principles will help considerably in the analysis and understanding of the complex steps involved in photochemical deterioration*.

TO ACTIVATE MOLECULES, RADIANT ENERGY MUST BE ABSORBED

Light exhibits the characteristic properties of both waves and particles. The corpuscular behavior of radiation is particularly apparent in the case of electromagnetic radiation of short wavelength. The particle, bundle, or "bullet" of radiant energy is called a *photon*, the energy of which is

given by the equation $E=h\nu$*. The energy of photons in the infrared range (long wavelength, low frequency) is seldom sufficiently great to induce the chemical reactions that are normally encountered in photochemical deterioration. As the wavelength of radiation gets shorter and shorter, however, through the blue and violet region of the visible spectrum and into the ultraviolet, the photons possess an increasing amount of energy and may induce photochemical changes such as will be considered below.

One of the key principles of photochemical phenomena is the Grotthus-Draper law. This states that only radiation that is absorbed by a substance may cause a chemical reaction. This, of course, is axiomatic: light must be absorbed, or "taken up," by a substance in order to act upon it**.

Why should radiation be absorbed by some molecules and not by others? Sir William Bragg, in *The Universe of Light*, uses the analogy to tuning forks which can be set in vibration when sound waves of the appropriate frequency pass through them. In a similar manner, certain musical instruments possess strings or resonant chambers which are not directly touched, but which are set in sympathetic vibration when other parts of the instrument are played upon. Correspondingly, it may be said that molecules tend to absorb energy when their electronic system is in tune with a particular frequency of light that passes through them.

THE PRIMARY PROCESS

When a photon is absorbed by a mole-

* The symbol ν stands for the frequency of the radiation, which is inversely related to the wavelength; h is Planck's constant, a number that relates the units of frequency to energy, equal to 6.6×10^{-27} erg-sec. The equation will yield the energy of the photon in terms of kilocalories per gram molecular weight (kilocalories per 6.02×10^{-23} bonds or photons) if used in the form $E= 2.86 \times 10^4/\lambda$, where the wavelength of radiation, λ, is in millimicrons. Values thus calculated for the energy of radiation at different wavelengths are given in Figure 1.

** Photochemical processes are so complex that this principle does not always appear to be obeyed. Hence, although the principle seems obvious, some authors refer to it as a "rule" rather than a "law."

cule, the energy thus supplied is said to excite the electronic system of the molecule or to "activate" the molecule. The excited molecule may then lose the absorbed energy (a) by heat, (b) by the emission of radiant energy in the form of fluorescence, (c) by undergoing a chemical change within the molecule, (d) by the breaking of chemical bonds, or (e) by collision and transfer of the energy to another atom or molecule. There are a number of more subtle ways in which the energy can be lost, but it is essentially the acquisition of the energy and its loss through these five principal ways that is considered to be the *primary process* of photochemistry.

One of the fundamental laws of this process is the Stark-Einstein law, also known as the *law of photochemical equivalence*. This law states that one atom or molecule is activated for every photon that is absorbed. To study the details of a photochemical reaction, the chemist often looks at the products of the reaction to determine the number of chemical transformations that have occurred for a given number of photons absorbed. Thus, if one molecule is changed or decomposed for every photon of light absorbed, the photochemist says that the *quantum yield* or *quantum efficiency* is equal to 1, just as predicted by the Stark-Einstein law.

The photochemical processes in the deterioration of paints, varnishes, and textiles are highly complex. For this reason, the quantum efficiency of the overall photochemical effect is often very much lower than 1*. For example, the quantum efficiency has been found to be only about 0.002 in the bleaching of certain dyes by light (5). That is: two dye molecules are bleached for every 1000 photons that are absorbed. In another example, it was found to be only 0.03 in the tendering (embrittlement) of certain textiles (1). Quantum

*For earlier reviews of photochemical principles, see J. Lodewijks, *Recent Advances in Conservation*, London, Butterworth, 1963, p. 7, and N. S. Brommelle, *Museums J.* 62: 337; 1962.

*Photons of low energy are frequently not efficient in giving rise to chemical change and the quantum efficiency may fall off at long wavelengths. This is the explanation usually given for such behavior as the decrease in the National Bureau of Standards' "factors of probable damage" at longer wavelengths. Certain types of photochemical reactions can also exhibit quantum efficiencies greater than 1.

yields as low as 10^{-4} and 10^{-5} have been reported for the deterioration of plastics and oil vehicles (20)(30).

It is the *energy* of the photons that are absorbed that brings about photochemical change. Lowering the intensity of illumination lowers the number of photons per minute, but does not alter their energy, for this is a function of their wavelength. As a consequence, there is theoretically no threshold of *intensity* of light below which photochemical reactions will cease to take place*. This conclusion is of considerable importance to the museum curator. No hope can be extended to him that, if sensitive objects are exhibited under an intensity lower than a particular level, photochemical deterioration will be arrested. At low intensities, the processes of photochemical deterioration will be retarded, but they will not be arrested.

An important generality is based on the above concept. This is that the net exposure, which influences the total amount of photochemical damage, is represented by the product of the intensity of the illumination times the time, other factors being equal. In other words, 1000 footcandles of intensity for 1 hour is considered to produce as much damage as 10 footcandles of the same radiation for 100 hours. This is because the product in each case is the same: 1000 footcandle hours. This concept is referred to as the *principle of reciprocity*.

It is of importance in connection with the museum problem that the research investigator be aware that the reciprocity principle is not always precisely followed. There are theoretical reasons why the reciprocity relationship may occasionally fail. In addition, the high intensities of illumination employed in accelerated testing frequently raise the temperature of the samples and lower their moisture content. Such an

alteration of conditions often accounts for the apparent failure of the reciprocity principle. Moreover, discontinuous exposure, that is, exposure under alternate conditions of light and dark, may occasionally give results that are different from those obtained under continuous exposure. This behavior has been observed in the case of the National Bureau of Standards' light-sensitive papers, for example (26).

In describing the primary process, five principal modes of energy dissipation were noted. Dissipation of the absorbed energy perhaps occurs most commonly through (a) conversion to heat, or (b) fluorescence. Neither of these modes gives rise to photochemical changes. On the other hand, (c) a change in chemical structure induced within the molecule by the absorption of light may enable the molecule to react more readily with oxygen, water vapor, etc. In a fourth way, (d) chemical bonds may be broken.

The literature on photochemical processes often compares the energy of chemical bonds with the energy of the photons in a simple chart, as shown in Figure 1. It is intended that one may readily see from such a chart that radiation of short wavelength is sufficiently energetic that it can break or "dissociate" a number of chemical bonds of lower energy. In spite of the frequency with which such charts are presented, a direct breaking apart of molecules may not be the predominant effect in the deterioration of solids and liquids activated by visible and the near ultraviolet radiation. Far more often, collision and transfer of energy with neighboring molecules takes place. This was listed as the fifth mode (e). Collision with neighboring molecules may dissipate the excitation energy so thoroughly that the quantum efficiency falls off. But, of particular significance are the cases in which the transfer of energy starts a chain of chemical events: the so-called secondary processes in photochemistry.

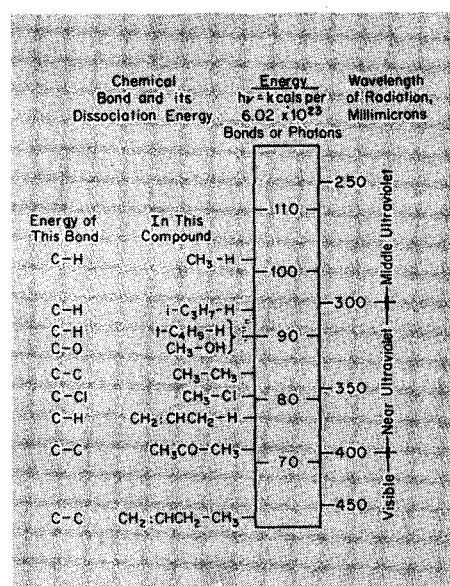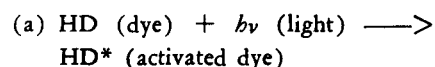## SECONDARY PROCESSES

Some typical reactions that occur in

FIGURE 1

A chart relating the energy of radiation of different wavelength to the energy of various chemical bonds
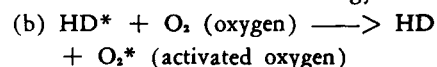
secondary processes are outlined in the following example of the formation of hydrogen peroxide on dyed cloth.
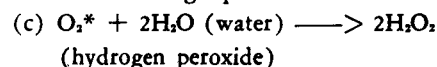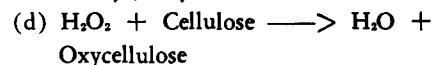
Primary Process:
Excitation
(a) HD (dye) + $h\nu$ (light) ——> HD* (activated dye)
Transfer of excitation energy
(b) HD* + O_2 (oxygen) ——> HD + O_2* (activated oxygen)

Secondary Processes:
Excited oxygen converts water to hydrogen peroxide, summarized in the following equation:
(c) O_2* + $2H_2O$ (water) ——> $2H_2O_2$ (hydrogen peroxide)
Ordinary chemical reactions between hydrogen peroxide and cellulose, or the dye, may follow.
(d) H_2O_2 + Cellulose ——> H_2O + Oxycellulose
and/or
(e) H_2O_2 + HD ——> H_2O + HOD (bleached dye).
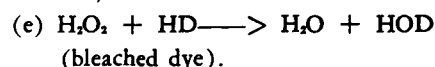
These equations are intended to show that, in the primary process, a molecule of dye, HD, is activated by absorption of light having energy, $h\nu$. The asterisk signifies

*In practice, there are a number of investigators who have reported that they have found intensities below which no reaction will take place. But, upon careful study, most such findings have been shown to be in error. For example, certain reactions may proceed at a negligible rate at low intensities, but proceed at a measurable rate in sunlight outdoors when the intensity is such that the samples attain a temperature higher than normal.
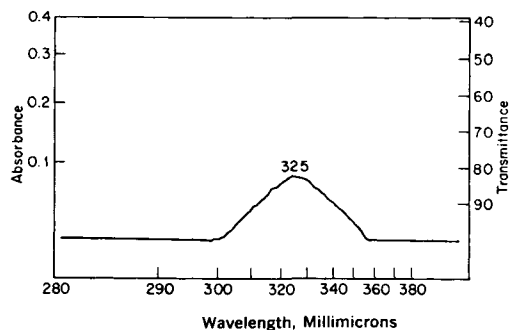
FIGURE 2

Microphotometer trace of the activation spectrum of a phthalic-maleic polyester resin, showing peak of photochemical deterioration at 325 millimicrons (Hirt, Searle, and Schmitt. *SPE Transactions* 1: 21-25; 1961)
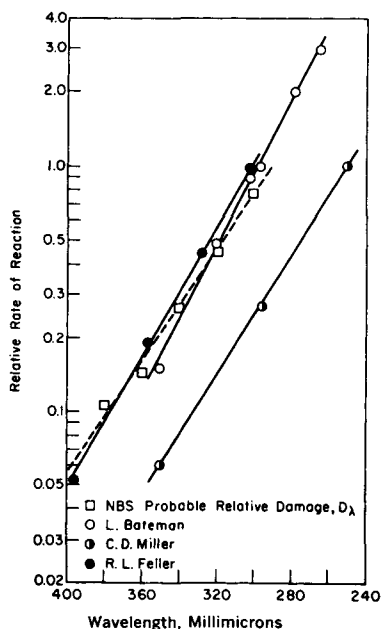

FIGURE 3

Data of several authors showing that the relative rates of certain types of photochemical reactions increase sharply with a decrease in the wavelength of radiation

a molecule in an activated or excited state. The energy of the activated molecule of dye can be transferred to oxygen, as indicated in equation (b). Through a complex series of reactions, which are merely summed up in a single step (c), the activated oxygen molecule is considered to be able to convert water to hydrogen peroxide.* The last two equations indicate that hydrogen peroxide can then attack either the cellulose of the cotton fibers or the dye. This relatively simple example, taken from a publication by Egerton, illustrates the complexity of photochemical processes: here, three different secondary reactions are involved (9).

The primary process is generally little dependent upon temperature. Any one of the steps in the secondary processes may be considerably dependent, however. For this reason, it is often difficult to "accelerate" photochemical deterioration in a completely satisfactory manner. Raising the temperature of the samples, for example—which usually occurs in most "accelerated aging" tests—does not necessarily speed up the various secondary processes each to the same extent.

The above chemical equations demonstrate why the quantum yield of the overall photochemical effect (the number of molecules affected for every photon absorbed in the primary process) may not be equivalent: after going through many intermediate steps, it may not be that one molecule of dye will be bleached, for example, for every photon (hv) involved in the first step (a).

In the example, one can also see why the presence of oxygen and water vapor profoundly influences many photochemical reactions: these substances are often directly involved in the secondary steps. When water is not consumed in such a process**, it is said to have a "catalytic" action. That is, its presence is able to

*Analogous to the dye, zinc oxide in textile fibers is able also to lead to the formation of hydrogen peroxide through a similar series of steps. See G. S. Egerton, *J. Textile Inst.* 39: T305; 1948.

** It is regenerated again in steps (d) or (e).

speed up the oxidation of the cellulose or the dye, yet it, itself, is not consumed.

A final and most significant point must be mentioned: if molecules are destroyed (for example, if the oxygen should break off pieces of molecules and convert them to volatile gases, such as carbon dioxide, water, and formaldehyde), the molecules would then be irreversibly altered and could not be simply put together again. To be sure, embrittled fibers can be consolidated by adhesives, but the broken chains of the fiber molecules themselves cannot be joined again as before. Once faded, most dyed objects cannot be converted back to their original color. Linseed oil broken down into volatile components cannot be reconstituted. The museum curator should realize that, on a fundamental chemical basis, *photochemical damage is practically irreversible damage.*

SUMMARY

The short wavelengths of visible and ultraviolet radiation are the most energetic and generally represent a greater photochemical hazard than radiation of longer wavelength. The primary process in photochemistry is the absorption of radiant energy by an atom or molecule and the dissipation of this energy. Molecules thus "activated" by light may undergo chemical changes within themselves or they may trigger off a number of secondary chemical processes. The latter result accounts in part for the complexity of photochemical reactions and for the reason why such substances as water vapor and oxygen often become directly involved. For a given type of illumination, the total exposure is considered to be a product of the intensity times the time. Lowering the intensity of light retards the rate of deterioration, but does not arrest it. Photochemical damage is practically irreversible damage.

Effect of Light on Varnishes and Paint Vehicles

In considering each class of material here and in future reviews, an attempt will be made to answer the following questions:

What is the particular action of light: fading, embrittlement, discoloration? Approximately what exposure, in terms of footcandle hours or other standards (13), is necessary to cause a given degree of change? What is the significance of temperature, of humidity, and of the wavelength of radiation, particularly the ultraviolet? What are the intrinsic and extrinsic factors that influence the photochemical action?

INFLUENCE OF WAVELENGTH

Light can hasten the oxidation of organic coatings, leading to yellowing, shrinkage, erosion of the surface, and changes in their sensitivity to solvents. The shortest wavelengths of radiation are generally the most effective. Since coatings tend to absorb shorter wavelengths more than the longer, it follows that the most active radiation seldom penetrates deeply. The most severe deterioration of the vehicle usually takes place on the surface.

Hirt, Searle, and their associates have recently developed a direct method to determine the wavelengths in the sun's spectrum that produce the maximum photochemical effect (23). Figure 2 illustrates a typical determination, giving what the authors call an "activation spectrum" for discoloration. The maximum effect occurred at 325 millimicrons, falling off below that because of the decreased energy in the sunlight, and above that, because of decreased absorption by the coating.

Figure 3 presents Miller's data on the relative effectiveness of various wavelengths in causing the degradation of an alkyd paint (30). In a thorough investigation, Miss Miller demonstrated that the degradation took place principally on the surface and that the reciprocity principle held well. She also showed that the mechanism of deterioration induced by long wavelength radiation was different from that induced by short. It can be seen in Figure 3 that her findings regarding the effectiveness of various wavelengths are similar to the National Bureau of Standards' "factors of probable relative damage" used in the
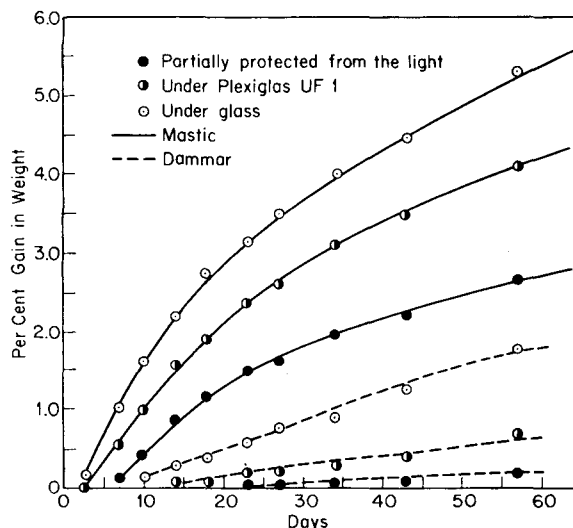
Gains in weight of pulverized dammar and mastic resins under daylight fluorescent lamps at approximately 240 footcandles intensity

Harrison report (21)(33). Bateman's data on the evolution of hydrogen gas when rubber is irradiated and the author's data on the tendency of certain methacrylate resins to become insoluble, also shown in Figure 3, follow much the same relationship (2)(14).

EFFECT ON THE VEHICLE

FitzGerald studied the evolution of volatile products from films of alkyd drying-oils and showed how the loss of these components led to shrinkage (18). Bullett and Rudram have since demonstrated that, under accelerated-weathering conditions, the loss of volatile material from linseed oil, stand oil, copal-oil varnishes, and long- and short-oil alkyds decreases with the content of oil in the vehicle (7). Payne has proposed a mechanism for the breaking and degradation of the polymer molecules in oils (36), and Blom and Krumbhaar have been able to photograph the stresses that are set up in films as they deteriorate (3)(4). Many of these and related changes of films with age, such as shrinkage, yellowing, increase in solvent resistance, etc., were the subject of a detailed investigation by the Federation of Paint and Varnish Production Clubs, published in 1958 (6).

The increase in the refractive index as linseed oil ages can lead to the formation of pentimenti (27). Exposure of light may hasten this change.

EFFECT ON VARNISHES

Natural-resin varnishes usually are readily oxidized upon exposure to light. The oxidation of rosin has been reported by Chinchin (8) and by Launer and Wilson (25); the oxidation of dammar and mastic resins, by Mills and Werner (31) and by the author (12). Figure 4 presents the results of some experiments at Mellon Institute in which a gain in weight of the latter two resins was observed during a total exposure of about 340,000 footcandle hours under "daylight" fluorescent lamps (15). This gain is assumed to be evidence of rapid oxidation. The effectiveness of the Plexiglas UF-1 ultraviolet filter in this experiment indicates that the gain is hastened by ultraviolet light.

The loss of solubility of certain methacrylate resins through the mechanism of crosslinking is most sensitive to the short wavelengths of radiation, as indicated by the author's data in Figure 2 (14)(17). In one series of tests under "daylight" fluorescent lamps, an exposure of 8 to 10 million footcandle hours produced 50 to 80% insoluble matter in films of the isoamyl and n-butyl polymers (14).

Oxidation of natural and synthetic resins generally means that "stronger" solvents are needed to remove the aged films. Figure
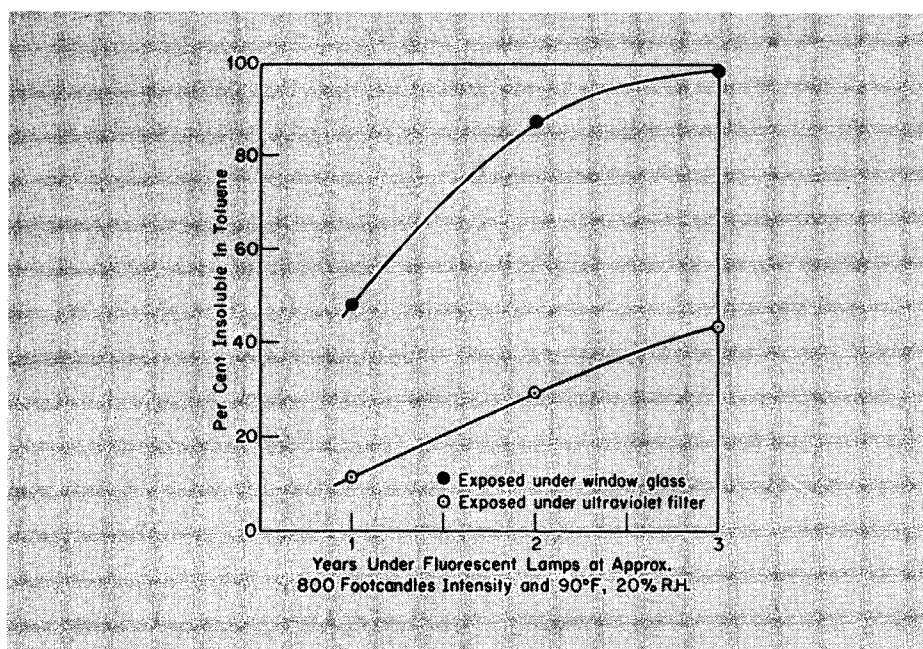
FIGURE 5

Rise of insoluble matter in dammar stand-oil varnishes
containing 20% oil by weight

5 indicates the decrease in solubility of a dammar stand-oil varnish in toluene upon exposure to fluorescent lamps. The observed increase in the insoluble fraction is apparently due to oxidation and not to a rise in crosslinked material: at the end of three years the films were still soluble in acetone to the extent of 95% or greater (15). A similar increase in resistance to solvents can occur with methacrylate polymers (14).

YELLOWING AND BLEACHING

The yellowing of oils has been extensively studied. Moore developed an equation which summarizes the essential findings of this research, giving the relationship between the amount of yellowing and the composition of the unsaturated fatty acids in the drying oil: $Y = K' + K(D + 5T + 3C)$, where D is equal to the percentage of dieonic acids present, 5T is equal to five times the percentage of trieonic acids, and 3C is equal to three times the percentage of conjugated fatty acids (32). Moore also made observations on the rate of yellowing.

Exposure of paints and varnishes to light can lead to both yellowing and bleaching. Blue light apparently causes the least amount of yellowing of oil-based paints and enamels, followed by green and red (46). Infrared radiation causes the greatest yellowing. Pfund determined precisely that the bleaching action fell off as the wavelength was increased above 290 millimicrons, yet still took place at 490. At 600 millimicrons, no bleaching was observed (37).

VEHICLES OTHER THAN RESIN-OIL

Light can, of course, affect vehicles such as glue, starch, and casein. It is perhaps in studies of the deterioration of size on paper that action of light on glue has received the most attention. Whelan and Peat have discussed the degradation of starch (47). The effect of light on bitumen was investigated long ago by Maxmillian Toch (45). He found that blue light caused greater embrittlement and cracking than green. Red light caused little change. A modern study of the deterioration of

asphalts can be found in the work of Wright and Campbell (48).

THE ROLE OF PIGMENTS

Because pigments block the passage of light, they generally provide considerable protection against the photodegradation of the paint vehicle (11). A few pigments, however, especially certain forms of titanium dioxide and zinc oxide, can hasten the deterioration of the vehicle. This will be discussed in a later publication concerning the action of light on pigments.

SUMMARY

Ultraviolet and the short wavelengths of visible radiation can bring about a number of changes in varnishes and paint vehicles. Pigments usually offer considerable protection to the bulk of the vehicle, but the short wavelengths of radiation readily attack the upper surface. The loss of volatile fragments from oils and resins during exposure leads to a decrease in weight, erosion of the upper surface, and shrinkage of the coating. Varnishes tend to become more resistant to the action of solvents, either through oxidation or through the formation of a crosslinked type of molecular structure. The formation of pentimenti in oil paints may also be hastened by exposure to light.

Effect of Light on Paper

INFLUENCE OF WAVELENGTH

Cellulose does not absorb visible radiation and for this reason, one might at first expect that it would not be affected by wavelengths greater than 400 millimicrons. Yet, Launer and Wilson (25) have reported on the effect of radiation from 330 to as high as 440 millimicrons, and both Richter (39) and Kohler (24) have reported on the effect of radiation between 400 and 460 millimicrons. Rather than the cellulose itself, it is perhaps glue, rosin, and other constituents of ordinary paper that are able to absorb the violet and blue radiation and to sensitize the paper to deterioration. Be that as it may, the activity of light

On page vii of the article on "The Deteriorating Effect of
Light on Museum Objects" in the June, 1964, Technical Supplement of
Museum News, there is a statement which can be easily misinterpreted
and lead to undue concern. At the top of the second column on that
page, it is said that ". . . once exposed to light, paper may deteriorate
at an accelerated rate when it is removed from the light and stored. In
other words, exposure to radiation is able to sensitize paper so that it
exhibits an increased rate of deterioration upon subsequent storage."
What is meant by this statement is that experimenters have found that, if
the open pages of a book, for example, were exposed to the light and the
book was subsequently taken off exposure and stored back on the shelf,
those pages which had been exposed to light may deteriorate at a faster
rate than the pages which had not been exposed.

The statement does not mean that, once exposed to the light,
the rate of deterioration becomes even greater than it was under the
light. Poor grades of paper deteriorate even in the dark. The evidence
of the investigators was that the paper that had been exposed to light
deteriorated faster than the ordinarily-expected rate in the dark. That
is, faster than the same type of paper would deteriorate in the dark if
it had never received any exposure to light.

It is a problem for the investigator, in considering what light
may do to objects, to wonder whether those materials which have been exposed
to light might not deteriorate, when subsequently stored, at a rate slightly
faster than they would otherwise do if they had never been exposed. Experi-
mental indications coming in from the research on paper seem to indicate
that this is true in the case of ordinary or low grade paper. The whole
subject, however, is something that must be carefully studied from the
museums' point of view. The purpose of a literature search of this type
is to uncover just such points that require further attention and research.

<div align="right">R. L. Feller</div>

certainly falls off rapidly at the higher wavelengths. In the deterioration of low grade paper, for example, the National Bureau of Standards' "factors of probable relative damage" were found to be only one-tenth as great at 480 millimicrons as at 400 (33).

EXPOSURE NECESSARY TO CAUSE DETERIORATION

Serious deterioration of paper is produced in 50 to 100 hours of exposure to full sunlight, an exposure of about 400,000 to 1 million footcandle hours, or 3600 to 9000 Langleys (39). It is difficult, however, to judge the significance of this observation in terms of exposure in a museum. This is because the temperature of the samples is increased during exposure to direct sunlight and the deterioration of paper is markedly influenced by temperature as well as by humidity. The influence of temperature is of such importance that the heating of paper is used as an accelerated-aging test to predict its long-term durability.

Control of the temperature of the sample has frequently been neglected in accelerated-exposure tests. This has led to many experimental results that cannot be readily interpreted in terms of room conditions. With this problem in mind, Launer and Wilson built special equipment to expose paper to the light of a carbon arc in such a way that the temperature of the samples was kept at 30°C. From their results, a rough estimate may be made that rag papers can lose 25%, and soda-sulfite papers 15 to 50%, of their resistance-to-folding after an exposure at 30°C (86°F) and 58% R.H. to about 1,700,000 foot-candle hours of 6500°K daylight.*

A finding of importance to the museum curator, verified by these authors and others, is the fact that, once exposed to light, paper may deteriorate at an accelerated rate when it is removed from the light and stored (25)(44). In other words, exposure to radiation is able to sensitize paper so that it exhibits an increased rate of deterioration upon subsequent storage.

INTRINSIC AND EXTRINSIC FACTORS THAT INFLUENCE THE DETERIORATION

Papers of high quality are much more stable than those of low*. Launer and Wilson found that papers decreased in stability in the order: new-rag, refined sulfite, old-rag, soda-sulfite, and newsprint. Paper containing lignin was particularly unstable to light.

The presence of dyes in paper also increased the extent of deterioration in certain cases. The sensitivity of new-rag papers was found to be markedly affected by the presence of acid in the rosin size; old-rag and soda-sulfite papers were less affected. Richter reported that sized papers deteriorated faster than water-leaf papers when exposed to sunlight, but Launer and Wilson found that rosin did not affect the stability of any paper as long as the acidity was low.

In the absence of water vapor and oxygen, there is reduced scission of the cellulose molecules by radiation in the near ultraviolet (25).

YELLOWING AND BLEACHING

The processes of both yellowing and bleaching go on at the same time. Launer and Wilson clearly demonstrated that paper yellowed when heated during exposure to light, but was bleached when kept at a low temperature. The net result depended on whether the changes caused by light or by heat predominated. Lignified papers discolored, however, even when no heating of the paper occurred. In groundwood papers, bleaching apparently is caused by wavelengths longer than 385 milli-

*The superior quality of the paper is in a large measure indicated by the content of alpha cellulose.

microns, yellowing by shorter wavelengths (34).

Launer and Wilson found that the yellowing that had been induced by heat, even to the extent of scorching, could be bleached by exposure to light. This could again be nullified by further heating of the paper. They cautioned, however, against any hasty suggestion that light should be used to bleach discolored documents, since it also causes deterioration of the cellulose.

The complex reactions that take place during discoloration—the "color reversion" or the so-called "brightness reversion" of paper—have been reviewed by several authors (28)(35)(43) and have recently been further elucidated by MacMillan (29).

DETERIORATION OF SIZE

Light can cause deterioration of the size. Violet, blue, and yellow wavelengths have proven to be the most active; red, the least (22)(49). Upon exposure to sunlight, rosin- and starch-sized papers have been found to be less sensitive to the change in writing qualities than glue-sized (39).

SUMMARY

Whereas the best grade of paper is perhaps reasonably stable to light, the presence of lignin, rosin, and other materials can hasten yellowing and embrittlement. The shorter wavelengths of light are more destructive than the longer. Once irradiated, paper is more sensitive to deterioration upon subsequent storage. The rate of deterioration is sensitive to temperature, so much so that heating samples in an oven is a standard test to "accelerate the age" of paper.

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