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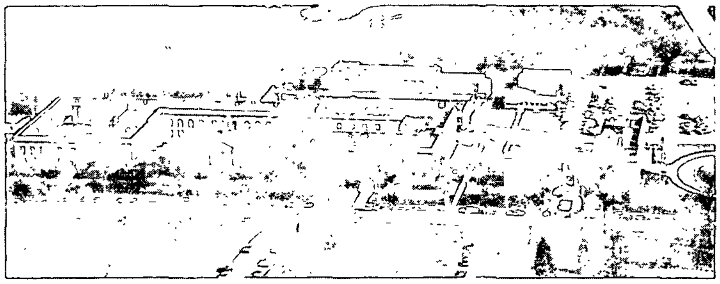

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VACUUM PHOTOSIZING OF CELLULOSE

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PHOTOSIZING OF CELLULOSE WITH OLEFINS

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INTRODUCTION

The sizing of paper greatly expands its end use capabilities. Conventional sizing agents have several shortcomings: Alum in rosin sizing reduces the lifetime of the paper due to acidic decomposition, and sizing agents which are not chemically bonded to the sheet allow interactions with moisture to gradually lessen the effectiveness of the sizing agent. Excessive amounts of material are usually used in an attempt to overcome this problem.

Chemically bonded sizing agents on the other hand are much more effective. Very small amounts of chemically bonded material, well distributed, can give a high degree of sizing and the effect is generally more permanent. A new method of producing these chemical bonds, described in the following paper, is by ultraviolet irradiation.

This method, in addition to opening up the possibility of new technology, might also prove useful in studying the surface properties of papers that have partial monolayers of hydrophobic material bonded to the surface or in studying the self-sizing of absorbent papers during storage.

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ABSTRACT

Ultraviolet irradiation of paper in the presence of olefins and in the absence of oxygen gave sizing of the paper. Under vacuum, vapor transport of olefin from one sheet to another occurred during irradiation. Subsequent extraction with four different solvents did not remove the sizing agent, providing evidence for a covalent bond to paper. Vycor filtered out the active wavelength unless benzophenone sensitizer was added. An upper limit on the amount of olefin incorporated into the paper was established as 0.2% of the weight of the paper. The sized paper lost some of its water repellency when overirradiated or subjected to surface abrasion. Two possible mechanisms are suggested for the photosizing.

INTRODUCTION

The report by Desai and Shields (1) describing the vacuum photosizing of cellulose simply by ultraviolet irradiation stimulated our interest in the area of photochemical sizing*. Although the chemical changes required to render the surface hydrophobic seemed rather extreme, the reported results were quite dramatic. Attempts to repeat their work, produced sizing only when rubber was a part of the apparatus. Thus, irradiations of paper in evacuated test tubes (quartz or pyrex) sealed with rubber stoppers gave complete sizing on the exposed side. Irradiations on a vacuum stage with a quartz window sealed with a rubber O-ring gave sizing in the vicinity of the O-ring. However, irradiations using test tubes connected to the vacuum line with ground-glass joints did not give sizing. If a rubber stopper was placed inside the tube with the paper, sizing occurred.

This led us to suspect that a volatile material from the rubber was causing the sizing effect in our systems. Although the volatile material which could be isolated from irradiation or warming (ca. 45°) a rubber stopper under vacuum showed only saturated aliphatic character in the nmr and infrared spectra, it seemed reasonable that a small amount of olefinic material could also be present in the volatile components of rubber. There is ample literature precedence for olefin formation in rubber degradation (2), and other work in these laboratories had shown that very small amounts of material chemically bonded to cellulose can give very large sizing effects (3).

RESULTS

Irradiation of Whatman No. 1 filter paper with a 450-watt medium-pressure mercury lamp through an evacuated quartz tube in the presence of olefins gave

*Sizing in this context shall refer to the rendering of a cellulose surface repellent to water.

sizing of the paper. High contact angles were obtained and the water droplets placed on the paper generally evaporated without wetting the sheet. Early experiments were carried out with straight-chain, terminal olefins of 12, 16, 18, and 20 carbons. Although sizing was obtained with all of these olefins, some variability of results was noted, indicating that the system was sensitive to operating parameters such as temperature, pressure, and olefin volatility. Much more reproducible results were obtained when a mixture of C_{16}, C_{18}, and C_{20} olefins was used. This blend covered a volatility range such that the system was much less sensitive to fluctuations in conditions from run to run.

In a typical experiment, a sample of paper (ca. 100 mg) was dipped into a hexane solution containing 2% (w/v) each of 1-hexadecene, 1-octadecene, and 1-eicocene, and the hexane was allowed to evaporate. Olefin uptake was ca. 10 mg. The sample was then placed in the quartz tube along with one or more undipped sheets, the tube was evacuated to 0.05 mm, and the sample was irradiated (typically 25 minutes) as described above. Under these conditions "complete" sizing was observed on the irradiated side of both dipped and undipped samples. Water drops placed on the paper did not wet the sheet, remaining on the surface until evaporation. Contact angles measured for such sheets ranged from 117 to 134°. The unirradiated side generally showed slight sizing.

Other irradiations were carried out under a variety of conditions. Under some conditions, sizing was obtained, while other conditions did not give sizing. These results are summarized in Table I. Irradiation with olefins under vacuum (entry I), as described above, gave sizing of dipped and undipped sheets. Similar irradiations, carried out in a nitrogen atmosphere (entry II), gave complete sizing of the olefin-dipped sheet and varying degrees of sizing of the nondipped sheets.

Vycor (λ >225 nm) and pyrex (λ >290 nm) filters (entries IX and X) removed the active wavelength range and no sizing was obtained. Similarly, air (>0.1 mm) quenched the reaction (entry XI).

Benzophenone shortened the required irradiation time through quartz by a factor of about two (entry III) and extended the active wavelength range to greater than 290 nm (entries IV and V). Benzophenone also gave sizing in the absence of olefins (entries VI-VIII), but longer irradiation times were required than for the combination of benzophenone and olefins.

The amount of olefin incorporated into the paper after irradiation was too small to be measured by weighing. A weight loss of about 3% was observed for sheets irradiated either in the presence or absence of olefins. This was presumably water loss; no significant difference in weight loss could be detected between sized and unsized sheets which had been irradiated. However, an upper limit could be indirectly placed on the amount of olefin incorporated. At the end of an irradiation, excess olefin which had not been pumped from the system had condensed on the cooler portions of the tube. Nine irradiations were carried out in succession without cleaning the tube between runs. In this manner, 5.6 mg of olefin was sufficient to size a total of 2.62 g of paper (on the irradiated side). This gave an upper limit of about 0.2% olefin incorporation, based on the weight of the paper. Since a significant fraction of the olefin almost certainly was removed by the vacuum, the actual amount is probably less.

The sized surface was somewhat fragile. Abrasion of the surface by scratching lightly with a pointed metal probe resulted in absorbency at the point of the scratch. Also, prolonged (2 hr) irradiation of a previously photosized sheet in the absence of olefins resulted in the loss of sizing.

The sizing agent could not be removed by solvent extraction. Several samples which had been sized photochemically with olefins were soxhlet extracted with benzene, toluene, acetonitrile, and decalin. At the end of these extractions, the paper was still sized.

DISCUSSION

The Role of the Vacuum

The above results indicate that the vacuum serves two purposes: the removal of oxygen and vacuum transport of olefin. If neither of these is required (e.g., nitrogen atmosphere and olefin-dipped paper), then the vacuum is not necessary. Desai and Shields found that in their system (1) an inert atmosphere was insufficient to give sizing and suggested that the vacuum might function to remove volatile decomposition products. However, if migration of a volatile material was important in their system, then vapor transport would be facilitated by the vacuum.

In the present work, migration of olefin (and benzophenone) was observed for irradiations carried out under vacuum. Irradiations in which the paper strips were held away from the walls of the tube by clips gave results equivalent to those in which the paper was in contact with the tube, indicating the quartz surface was not directly involved in the transport.

Nature of the Sizing Effect

The effects of surface abrasion and overirradiation are consistent with the sizing being close to the surface of the paper. It has been shown that irradiation results in cellulose decomposition predominantly on the surface (4). If it is assumed that cellulose decomposition is responsible for the loss of sizing upon overirradiation, either by loss of the hydrophobic groups via cleavage reactions or a masking of their effect by changes in the cellulose, then it can be inferred that the effect is localized on the surface.

The fact that the sizing material could not be removed by extraction with a variety of solvents is consistent with a covalent bond being formed between olefin and cellulose. Direct evidence for such a bond is difficult to obtain. In cellulose grafting studies, it is generally assumed that homopolymer will be soluble in an appropriate solvent while graft copolymer will remain attached to cellulose and thus be insoluble. A more direct proof of a chemical bond would be difficult to obtain due to the small amount of olefin incorpoated into the paper.

Mechanism for Photosizing

Two possible mechanisms come to mind. Free radicals are known to be produced upon ultraviolet irradiation of cellulose (5). These free radicals would be expected to react with olefins, as shown in Equation 1

$$\text{CELL-H} \xrightarrow{h\nu} \text{CELL}\cdot \xrightarrow{CH_2=CH-R} \text{CELL-}CH_2\text{-}\dot{C}H\text{-R} \qquad (1)$$

to form covalent bonds. The product radicals could then be quenched by the system, forming a monomeric graft, or react with more olefin to give a graft polymer on the cellulose.

The second mechanism involves light absorption by the olefin. Since olefins are known to form free radicals upon photolysis (6), this could be a source of hydrocarbon radicals. These hydrocarbon radicals could then combine with radicals on cellulose, which were formed either by photolysis or chain transfer, to produce a covalent bond.

The results described above are consistent with either mechanism. The observation that Vycor filtered out the active wavelength might imply that light absorption by the olefin is important, since cellulose absorbs at wavelengths greater than 225 nm (7). However, Kujirai (8) has shown that cellulose is more sensitive to the 184.9 nm component of a low pressure mercury lamp than to the 253.7 nm component in spite of the much lower intensity of the former. Phillips, et al. (5) found maximum radical formation of cellulose when irradiation was at ca. 360 nm. This, however, is probably a reflection of the spectral output of their high pressure mercury lamp and not cellulose sensitivity. A high pressure mercury lamp probably has a smaller percentage of the very short wavelength light than does the medium-pressure lamp used in the present work (9), although this will vary with the condition of the lamp.

The fact that benzophenone enhanced the reactivity of the system is also consistent with either mechanism. Since hydrogen abstraction reactions by carbonyl "impurities" in cellulose might be important in the formation of free radicals in cellulose (10), it is to be expected that benzophenone would enhance such reactivity by increasing the carbonyl content. However, benzophenone would also be expected to transfer triplet energy to the olefin. Although direct irradiation of olefins gives the singlet excited state and intersystem crossing to triplet is generally inefficient in olefins, hot ground states derived from both singlets and triplets of dienes have been invoked for fragmentation reactions (11). Such hot ground states would not, however, be important for the irradiation in the nitrogen atmosphere due to collisional quenching.

It is interesting to note that benzophenone gave photosizing, even in the absence of olefin. The fact that sheets dipped in benzophenone solution were not sized when irradiation was through Vycor or pyrex, even though other undipped sheets in the tube were sized, suggests that excessive absorption by benzophenone, perhaps in the form of crystals, minimized the interaction of excited ketone with cellulose.

The present work with olefins does not prove that a similar process is responsible for the sizing effect in the presence of rubber, especially in view of the fact that sizing could be obtained with rubber by irradiation through pyrex. Nor does it speak directly to the question of the nature of the effect observed by Desai and Shields (1). However, sizing in the presence of olefins might have more far-reaching implications than sizing in the presence of rubber.

EXPERIMENTAL

General

All irradiations were carried out with a Hanovia 450-watt medium-pressure mercury arc lamp. The distance from the center of the lamp to the paper was 10 cm. Unless otherwise indicated, all irradiations were done under a vacuum with a pressure of less than 0.05 mm (0.1 mm was inadequate). The vacuum was maintained by continuous pumping. Irradiations were done in quartz or pyrex tubes, as indicated, 3.0 cm O.D. x 42 cm long attached to the vacuum line by a ground glass joint using a minimum amount of vacuum grease.

For Vycor-filtered light, a Vycor filter was placed around the lamp and the quartz tube was used. Unless otherwise noted, irradiations were for 25 minutes with a new lamp or 60 minutes with an older lamp. Whatman No. 1 filter paper was used throughout.

Contact angles were measured with a Ramé-Hart contact angle goniometer. Sizing was evaluated qualitatively by placing small droplets of water (*ca*. 2 microliters) on the sheet. Sizing was said to be "complete" if the water did not penetrate the sheet during the 5-10 minute observation period. Unless otherwise stated, results given are for the exposed side of the paper.

Solutions for Dipping Paper

An olefin solution was prepared by dissolving 0.8 g each of 1-hexadecene, 1-octadecene, and 1-eicocene in 40 ml of hexane. Dipping strips of paper in this solution and allowing the hexane to evaporate resulted in the uptake of ca. 10% of the weight of the paper. Similarly, a 1% solution of benzophenone in 95% ethanol resulted in an uptake of ca. 5%. Most of the material left the paper during irradiation, since both dipped and undipped strips of paper lost 3% of their original weight (presumably moisture).

Determination of Upper Limit for Olefin Incorporation

A strip of filter paper was dipped in the olefin solution. The weight before and after indicated an olefin uptake of 5.6 mg. This strip was irradiated with two other, undipped strips under the usual conditions. All three strips were removed and three new, undipped strips were put in the tube. Nine such irradiations were carried out without cleaning the tube between runs. During this time, the olefin gradually migrated to the ends of the tube where it was cooler. A total of 2.62 g of paper was treated. In the first three irradiations, sizing was complete for all three sheets. In the last six irradiations, complete sizing was observed for the two strips closest to the ends of the tube (where more olefin was present) but only partial for the center strip. At the end of the series a very small amount of olefin could still be seen in the tube.

Irradiations in a Nitrogen Atmosphere

Olefin-dipped and undipped strips of paper were placed together in the quartz tube and oxygen was removed by pumping to 0.05 mm pressure and then filling the tube with nitrogen by means of a three-way stopcock. This was repeated for a total of three times. The final pressure was 630 mm, the partial vacuum being used to hold the joint together. Irradiation was for 25 minutes. This experiment was repeated several times. In all cases the dipped strips showed complete sizing. The undipped strips showed varying degrees of sizing.

Irradiations in the Presence of Benzophenone

In this series, one strip of paper was dipped in the benzophenone solution described above. Two other strips were placed in the tube with the first strip. For experiments with olefins, one of these two was dipped in the olefin solution. Irradiations were carried out in the usual fashion, as described in Table I.

Overirradiation of Sized Sheets

An olefin-dipped and undipped strip of filter paper were irradiated together under the usual conditions to give complete sizing on the irradiated side. The quartz tube was then cleaned thoroughly and the samples were irradiated further for two hours without olefin. The olefin-dipped sample absorbed water in 5-10 seconds while the undipped strip absorbed water in 1-5 seconds. Overirradiation for less than two hours destroyed sizing on the undipped strip to a greater extent than on the dipped one.

Solvent Extractions of Sized Paper

Samples of the photochemically sized paper were extracted by placing them in the upper part of a small Soxhlet extractor and extracting with solvent for two hours. This was done with benzene, toluene, decahydronaphthalene, and acetonitrile (1-hr extraction). The sizing was not lost by the extraction. Control samples of untreated filter paper were extracted with the hydrocarbons solvents and did not show any sizing.

Miscellaneous Control Experiments

Paper irradiated without olefin or benzophenone did not give sizing even after extended irradiation. Olefin-dipped strips did not show sizing before irradiation. Strips dipped in a 2% solution of 1-eicocene in hexane and then warmed to 45° for 30 minutes did show sizing, but this was removed by toluene extraction.

Irradiation of olefin-treated sheets in air, or at pressures of greater than 0.05 mm, did not give sizing. Irradiation in the presence of hexadecane under conditions which gave sizing with olefins, failed to size the paper.

Irradiation Without Contact with the Quartz Tube

Two clips were fashioned out of paper clips to hold the paper strips away from the tube. An olefin-dipped strip was placed in one clip and an undipped strip was placed in the other. Irradiation under vacuum with the usual conditions gave complete sizing of both strips.

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Table I. Conditions of Irradiations[a].

	Environment	Additive(s)	Filter	Result
I	Vacuum[b]	Olefins	Quartz	Sizing
II	Nitrogen	Olefins	Quartz	Sizing[c]
III[d]	Vacuum	Olefins + Benzophenone	Quartz	Sizing
IV	Vacuum	Olefins + Benzophenone	Vycor	Sizing
V	Vacuum	Olefins + Benzophenone	Pyrex	Sizing
VI	Vacuum	Benzophenone	Quartz	Sizing
VII	Vacuum	Benzophenone	Vycor	Sizing[e]
VIII[f]	Vacuum	Benzophenone	Pyrex	Sizing[e]
IX	Vacuum	Olefins	Vycor	No Sizing
X	Vacuum	Olefins	Pyrex	No Sizing
XI	Air[g]	Olefins	Quartz	No Sizing

[a] Irradiation time: 25 min unless noted.
[b] Pressure of 0.05 mm or less required.
[c] Sizing of olefin dipped sheet only.
[d] 10 Min irradiation.
[e] Sizing only of strips not dipped in benzophenone.
[f] 50 Min irradiation.
[g] 0.1 mm or Atmospheric pressure.