Light-Sensitized Crosslinking of Polyvinyl Alcohol by Chromium Compounds

B. DUNCALF and A. S. DUNN, *Department of Printing and Photography* and *Department of Chemistry, The Manchester College of Science and Technology, Manchester, England*

Synopsis

The insolubilization of polyvinyl alcohol by potassium dichromate on exposure to light has been investigated.   Ultraviolet spectrometry shows that secondary hydroxyl groups are oxidized to ketone groups but insolubilization is attributed to crosslinking of polymer chains by co-ordination of alcohol groups to "nascent" chromic ions formed by reduction of the dichromate.   Exposure to air saturated with water vapor eliminates the carbonyl absorption maxima from the ultraviolet spectrum of polyvinyl alcohol film but the spectrum can be restored by heating: this phenomenon is independent of the crosslinking reaction.

The insolubilization of films of such materials as glue, gelatin, and gum arabic by the action of light and an alkali dichromate is fundamental to processes for the preparation of blocks for illustrations in letter-press printing.   Though these photoengraving processes have been very widely used for at least eighty years the chemistry of the reactions which result in the "colloid" becoming insoluble have not been elucidated.

Briefly, practice in photoengraving is to place a zinc or copper plate which has been coated with a thin layer of "dichromated colloid" in contact with a negative of the photograph to be reproduced and to expose them, behind a glass plate, to radiation from an arc lamp.   The exposed areas become insoluble in water; the picture is developed by washing away unexposed material.   Inspection is facilitated by dyeing the film remaining with a suitable dye such as erythrosine (C. I. 45430).   At this stage the exposed film is still soluble in decinormal acid but it can be rendered acid-resistant by "burning-in," that is, by heating to a temperature of about 300°C.   The uncoated areas may then be etched away with acid leaving the positive photograph in relief as required for letter-press printing.

In the course of the last thirty years polyvinyl alcohol has become widely used in photoengraving because of greater convenience in use compared with the naturally occurring colloids, because it gives a better resist to acid in etching and because it is more easily "burnt-in" on zinc plates than the natural colloids—the lower temperature required is not liable to cause re-

crystallization of the zinc which gives rise to a fault technically described as "over-burning."

Previous suggestions on the chemistry of the photoengraving process have been reviewed elsewhere.[1] In the present experiments the first stage of the reaction has been studied with polyvinyl alcohol. Other "colloids" have been found to behave similarly.[2] It is hoped to study the second (burning-in) stage later.

EXPERIMENTAL

The polyvinyl alcohol used in most experiments was Gelvatol 20–30 obtained from Shawinigan Ltd. This contained 20 mole-% residual acetate groups, and, as its ultraviolet spectrum (Fig. 1) shows, had undergone some oxidation.[3] While the polyvinyl alcohol chain has predominantly a 1,3-glycol structure resulting from head-to-tail addition of vinyl acetate molecules, Flory and Leutner[4] have shown that 1,2-glycol structures resulting from head-to-head additions occur to an extent depending on the temperature of polymerization of about 1.5 mole-%. Polyvinyl acetate produced by radical polymerization at ordinary temperatures is highly branched.[5] Branches linked through ester groups are removed by hydrolysis, and polyvinyl alcohol produced from polyvinyl acetate which has been polymerized to only a low conversion is linear,[6] but it is possible that commercial high conversion samples may contain long branches linked through carbon to carbon bonds. To assess the effect of the residual acetate groups, acetate-free polyvinyl alcohol was used in some experiments. This was Gelvatol 1-90 containing approximately 1 mole-% residual acetate: it was not appreciably oxidized (Fig. 1).

Films were prepared from a casting solution consisting of a mixture of 10 volumes of a 15% (w/v) solution of polyvinyl alcohol and 1 volume of a $0.2M$ solution of potassium dichromate (Analar grade), the pH of which was normally adjusted to 6.05 initially with potassium hydroxide solution. Films were cast by a method similar to that used technically for coating plates by using a "whirler"—a turntable to which the plate to be coated can be attached which can be rotated horizontally at a range of speeds. Films were usually cast on Perspex (polymethyl methacrylate) plates since they could readily be detached from this material. When a supported film was required it was cast on a glass or silica plate. Casting on the whirler gave a more uniform film than spreading over a plate with a blade or casting on a mercury surface. It was essential that the Perspex plate should be thoroughly clean. The plate was cleaned by diluting a small quantity of the casting solution with an equal volume of water, wiping the mixture over the plate with cotton wool and washing it off with water. The plate was rotated at 200 rpm and a quantity of the solution poured on the center of the plate. Rotation was continued for 10–15 min. until the film which formed had dried. The thickness of the film could be varied by changing the speed of rotation or the concentration of the polyvinyl alcohol solution.
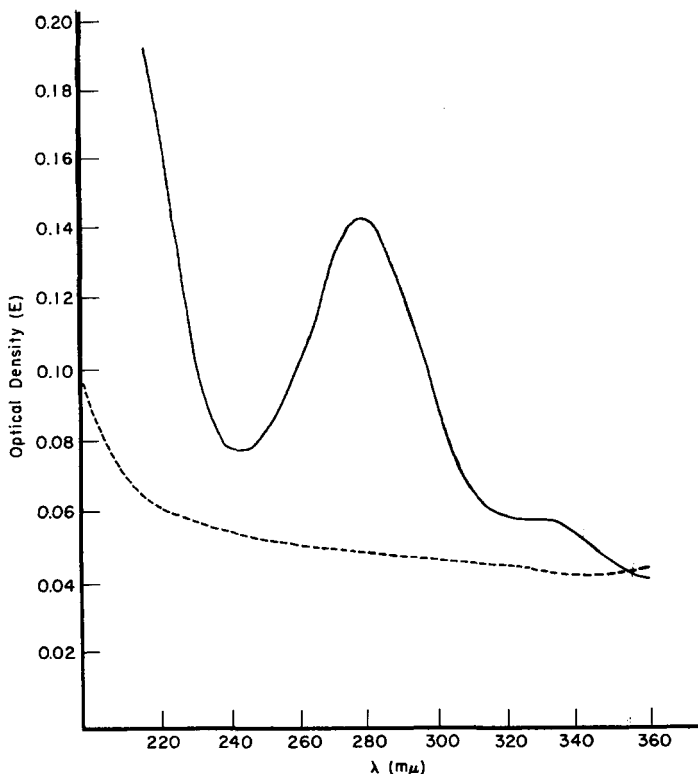
Fig. 1. Ultraviolet spectra of polyvinyl alcohol films (against an air blank): (———) containing 20% residual acetate groups; (- - -) containing 1% residual acetate groups.

The film could easily be peeled from the Perspex plate after first raising its edges with a razor blade or by lifting pieces of cellulose adhesive tape placed round the edges of the plate prior to casting. Films were about 0.003 mm. thick. Specimens were exposed at 1 m. from a carbon arc lamp operating at 30 amp. on a 45-v. supply.

RESULTS

Insolubilization of Film and Reduction of Dichromate

Films were exposed under standard conditions for various lengths of time. After exposures of more than 3 min. the film could not be dissolved completely. The specific viscosity of a 1% aqueous solution of the film after exposure increased (Table I) consistent with an increase in the average molecular weight due to a degree of crosslinking insufficient to render the film insoluble. The amount of dichromate which could be extracted from the film and the pH of a solution (or suspension) of the film at the same concentration as in the original casting solution were also determined.

Time, min.	η_{sp} (1% soln.)	pH (13.5% soln.)	Dichromate remaining, %
0	0.38	6.05	100
1	0.40	6.15	69.3
2	0.42	6.40	49.3
3	0.51	6.65	44.8
4	Insoluble	6.95	42.9
5	"	7.10	41.7
10	"	—	33.8
120	"	—	20.2

Tests on the insoluble film by the methylene blue method[7] were negative, indicating that the oxidation of the polyvinyl alcohol did not proceed so far as to produce carboxyl groups.

Insoluble film from which residual dichromate had been extracted was dissolved in 0.1N hydrochloric acid and reprecipitated by running the solution into acetone. The precipitate was insoluble in water and contained chromium.

Insoluble films could also be dissolved slowly by 0.1N sodium hydroxide solution, 0.5N potassium cyanide solution, 0.3N aqueous solution of ethylenediaminetetraacetic acid, mixtures of equal parts by volume water and pyridine, or of glycerol and pyridine.

Insolubilization of the film on exposure to light could be inhibited by incorporating at least enough ethylenediaminetetraacetic acid to combine with 75% of the chromium present; smaller amounts reduced the sensitivity of the film to light.

Ultraviolet Spectra of Films

The effect on the ultraviolet spectrum of the exposure of a dichromated film to light measured against a similar film without dichromate as blank is shown in Figure 2.

The spectrum of potassium dichromate in aqueous solution[8] varies with concentration because of hydrolysis:

$$Cr_2O_7^= + H_2O \rightleftharpoons 2HCrO_4^-$$
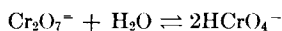
and with pH because of ionization of the acid chromate ion ($pK \sim 6.5^9$)

$$HCrO_4^- \rightleftharpoons H^+ + CrO_4^=$$

The effect of change of pH of the casting solution on the spectrum of potassium dichromate in polyvinyl alcohol film is shown in Figure 3. Figure 2 shows that absorption decreases with increasing exposure at wavelengths above 330 mμ but increases at lower wavelengths. Table I shows that the hydrogen ion concentration in the film decreases during exposure. Figure 3 shows that this would result in an increase in absorption at 370 mμ. The observed decrease is thus consistent with reduction of the dichro-
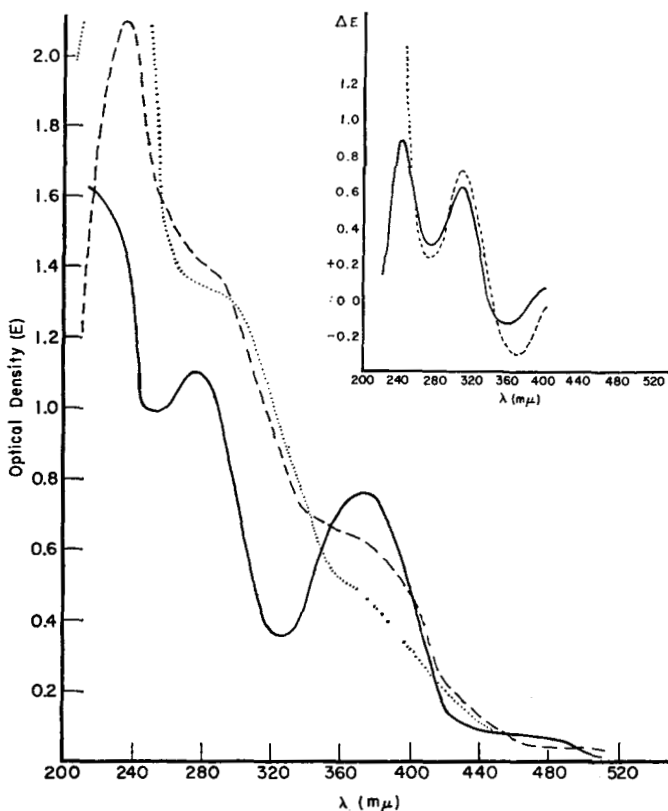
Fig. 2. Ultraviolet spectra of dichromated films before and after exposure: (——) film before exposure; (– –) film after 5 min. exposure; (- - -) film after 18 min. exposure. Inset: change in optical density (ΔE) on exposure: (——) 5 min. exposure; (- - -) 18 min. exposure.

mate. The increased absorption at wavelengths below 330 mμ must be attributable to the effect of oxidation of the polyvinyl alcohol, but the changes are masked by simultaneous changes in the absorption of the dichromate in the film. The changes are clearer in the spectra (Fig. 4) of films dissolved in acid after being precipitated from acid solution with alcohol to remove the residual dichromate. The intensity of the maxima at 210, 280, and 330 mμ attributed to ketone groups in the original film has increased. The nature of the groups formed in the oxidized alcohol is clearly demonstrated by preparation[3] of the derivative with 2,4-dinitrophenyl-hydrazone (Fig. 5).

Effect of Water on Exposed Films

Washing the insoluble exposed film with water was found to have a remarkable effect. The absorption maxima attributed to conjugated carbonyl groups disappear completely (Fig. 6). The same result can be
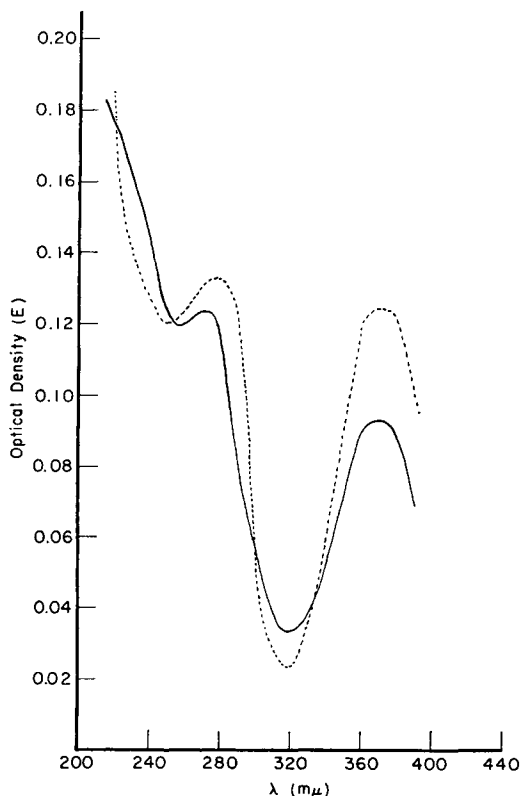
Fig. 3. Ultraviolet spectra of dichromated films at different pH values: (——) pH 5.74; (- - -) pH 7.08.

achieved merely by allowing the film to stand in an atmosphere saturated with water vapor (Fig. 7). It was considered whether this was due to a crosslinking process involving reaction of the carbonyl groups, but this is clearly not so because the spectrum can be restored by heating the film to 100°C. to drive off water (Fig. 7) and because soluble films containing carbonyl groups which have not been photoxidized behave similarly. Yet aqueous solutions of polyvinyl alcohol have an absorption spectrum similar to that of the films before washing or after heating. The origin of this phenomenon is obscure, but it is clearly irrelevant to the insolubilization of the films.

DISCUSSION

Nature of the Photosensitive Species

Only dry dichromated polyvinyl alcohol films are insolubilized by light. Though light of wavelengths longer than those absorbed by glass insolubilizes film, no increase in the viscosity of aqueous solutions of polyvinyl
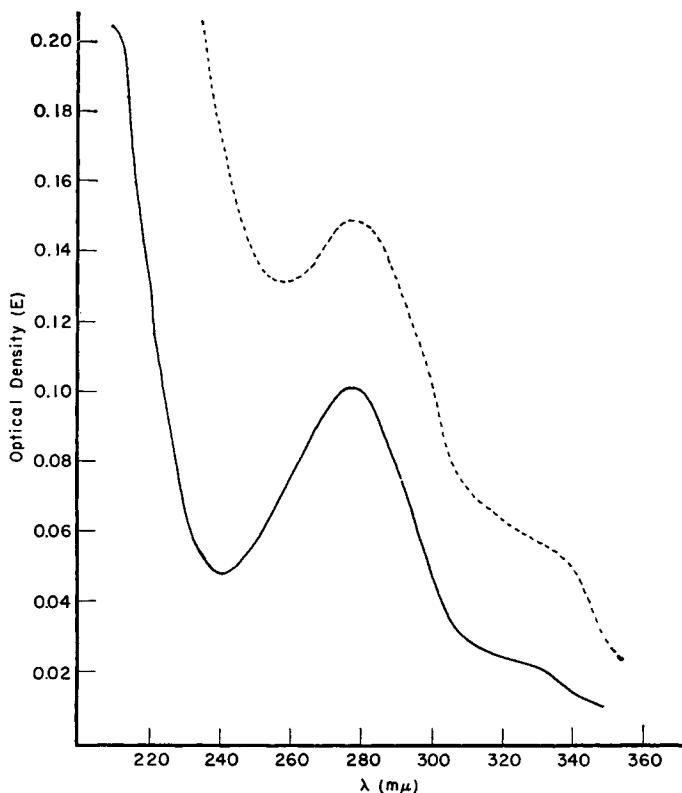
Fig. 4. Ultraviolet spectra of polyvinyl alcohol solutions in $0.02N$ HCl: (———) exposed in absence of dichromate; (- - -) exposed in presence of dichromate.

alcohol containing dichromate could be detected until after several hours' exposure under conditions in which film was rendered insoluble in 3 min. Nevertheless, alcohols in aqueous solution are photooxidized by dichromate, a fact which shows that oxidation and crosslinking are independent processes. Bowen and Bunn[10] found that primary and secondary alcohols could be photooxidized to the corresponding aldehyde or ketone in acid or neutral solutions but not in alkaline solution; in neutral solution a brown chromium compound was precipitated. The photosensitive ion was identified[11] as the acid chromate ion, $HCrO_4^-$, which is converted to inactive chromate ion, $CrO_4^=$, in alkaline solution ($pK_2 \sim 6.5$).[9] In an extensive series of papers, Westheimer and his co-workers[12-14] have given evidence that the thermal oxidation by chromic acid of isopropanol in dilute aqueous acid proceeds by intermediate formation of the ester, monoisopropyl chromate. Diisopropyl chromate has been prepared and is found to be photosensitive. Thus the chromate ester of polyvinyl alcohol may be the photosensitive species. Roček[15] has argued in favor of a mechanism for the thermal oxidation of alcohols involving the transfer of a hydride ion (rather than a proton) from the substrate to the chromic acid molecule which would not in-
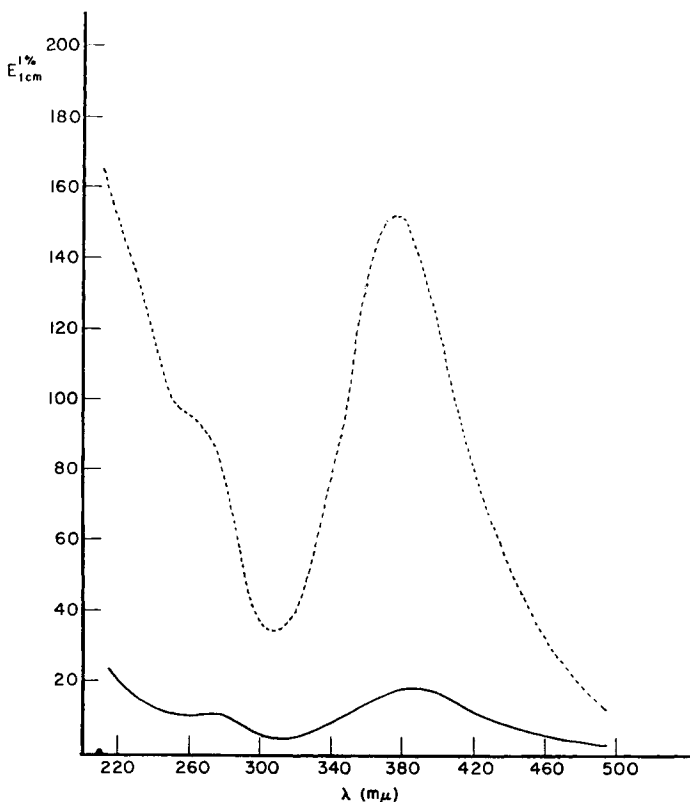
Fig. 5. Ultraviolet spectra of 2,4-dinitrophenylhydrazones of polyvinyl alcohols: (———) polyvinyl alcohol alone; (- - -) polyvinyl alcohol exposed in presence of dichromate.

volve the ester as an intermediate. Roček's discussion derives from the analogy with the thermal oxidations of hydrocarbons where ester formation is not possible. Westheimer[16,17] has criticized some of Roček's arguments. However, Weber and Ašperger[18] have found the photooxidation of glycerol by dichromate to have a negative energy of activation at high glycerol con-concentrations. This is explicable if the reaction mechanism involves an equilibrium (such as the formation of a chromate ester) and the equilibrium concentration of the photosensitive ester decreases with increasing tempera-ture. Thus it may be that the detailed mechanism of the photochemical and thermal oxidations of alcohols by chromium (VI) differs. No observa-tions on photooxidation of hydrocarbons by dichromate appear to have been published.

Product of Reduction of Dichromate

The ultimate product of reduction of the dichromate would be expected to be trivalent chromium though it is likely that the mechanism of the reac-tion will involve unstable ions of intermediate valency.[12] However, no
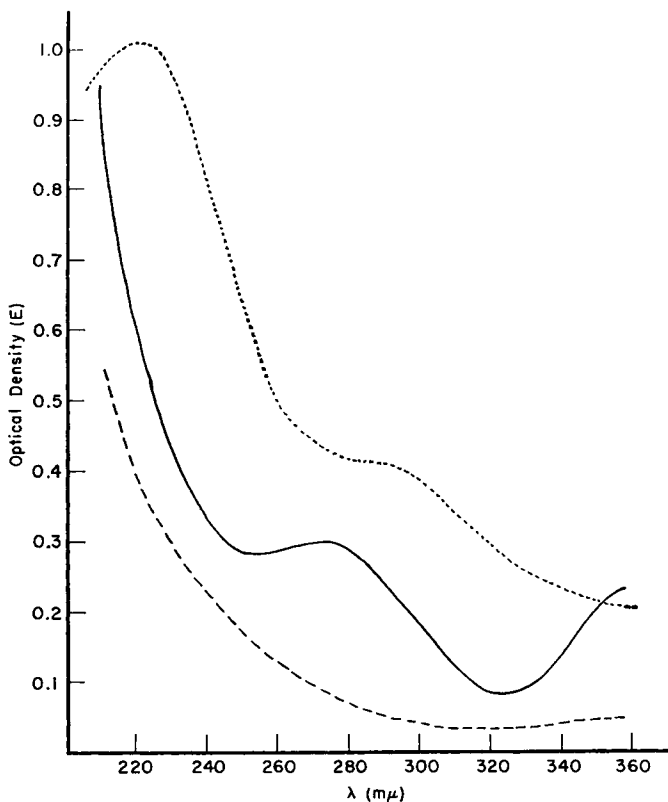
Fig. 6. Effect on ultraviolet spectra of washing exposed film: (———) film containing dichromate, unexposed; (- - -) film containing dichromate, exposed; (- -) exposed film washed with water.

chromic ions have been detected in exposed films.   Exposed films are brown in color.   A brown precipitate forms when alcohols are photooxidized with dichromate in neutral solution.   Some authors[19] have supposed this material to be chromium dioxide, CrO_2, but it seems more likely that it should be formulated as chromic chromate $[Cr(H_2O)_6]_2 (CrO_4)_3$ or as a basic chromic chromate such as $[Cr(H_2O)_5(OH)]CrO_4$.[20,21]   Some of the reduced chromium appears to form a compound of this type which apparently prevents reduction of all the dichromate present.

Oxidation of the Polyvinyl Alcohol

The carbonyl groups produced by photooxidation of the polyvinyl alcohol with dichromate are clearly similar to those present in most samples of polyvinyl alcohol (Fig. 4).   The nature of these carbonyl groups was first investigated by Clarke and Blout,[3] but recent evidence from a variety of sources[22–24] shows that their conclusions required modification in that introduction of a carbonyl group into the polyvinyl alcohol chain evidently
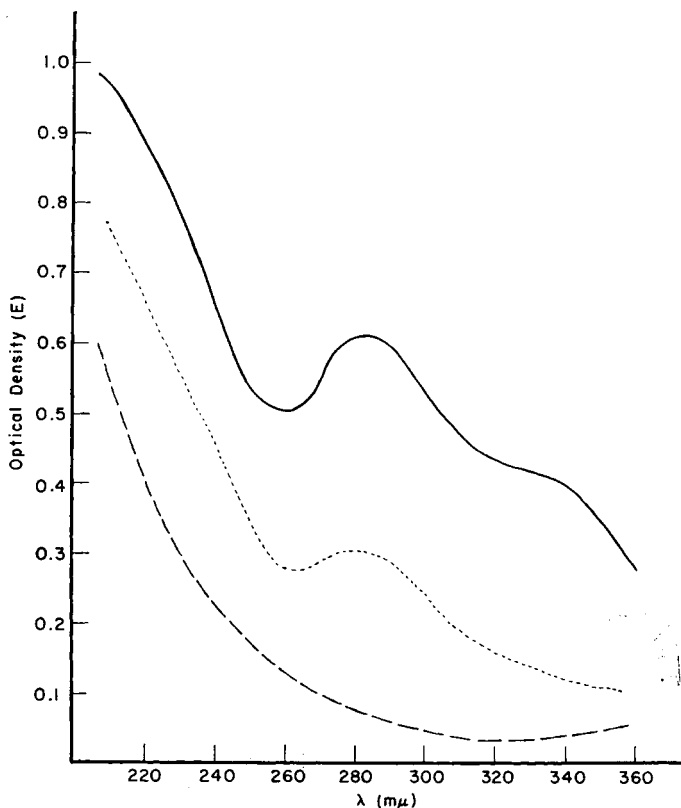
Fig. 7. Effect on ultraviolet spectra of heating exposed and" humidified" films: (– –) exposed film after humidifying for 20 hr.: (– – –) humidified film after heating for 35 min. at 100°C.; (——) humidified film after heating for 90 min. at 100°C.

permits facile dehydration of the adjacent —CH$_2$CH(OH) group with formation of chromophores of the type —(CH—CH)$_n$CO—, where $n = 1, 2,$ or 3. The position of the longest wavelength band in the absorption spectra of ketone 2,4-dinitrophenylhydrazones provides a criterion[25,26] of the existence of a double bond conjugated to the carbonyl groups. Table II

TABLE II

Comparison of Spectra of 2,4-Dinitrophenylhydrazones of Saturated and Unsaturated Ketones (in Alcohol) and Exposed Polyvinyl Alcohol (in Aqueous Alcohol)

Substance	Absorption maxima, mμ					Reference
Acetone	228		255		362		25
Methyl isopropyl ketone	228		255	280	362		25
Mesityl oxide	224		256	280		379	25, 26
α-Ionone	223	245	252	282		377	25
Acetyl cyclohexanone	228		255	280		377	25
Polyvinyl alcohol (oxidized)				280		377	

shows that the 2,4-dinitrophenylhydrazone of oxidized polyvinyl alcohol has a band at 377 mμ, the wavelength characteristic of unsaturated ketones. The conclusion that dehydration may proceed further to produce sequences of two or three unsaturated linkages is substantiated by consideration of the effect of heating on the spectrum of the exposed film. The relative change in absorption intensity is greatest at 330 mμ and greater at 288 mμ than at 228 mμ. Comparison with the wavelength of the principal absorption band of model compounds (Table III) shows that, while further dehydration on

TABLE III

Comparison of Absorption Maxima of Oxidized Polyvinyl Alcohol Film with Those of the K-Bands of Model Ketones and Aldehydes in Alcohol

Substance	Absorption maxima, mμ			Reference
$CH_3COCH{=}CH_2$	215			27
$CH_3CH{=}CHCHO$	217			28
$CH_3(CH{=}CH)_2COCH_3$		271		29
$CH_3(CH{=}CH)_2CHO$		270		28
$CH_3(CH{=}CH)_3CHO$			316	28
Polyvinyl alcohol (oxidized film)	220–230	280–290	300–330	

heating increases the concentration of all types of unsaturated ketone groups, this observation would be consistent with the development of doubly and triply unsaturated groups at the expense of groups with lower degrees of unsaturation. As to the effect of water sorption on the spectrum, it is clear that this destroys the conjugation of the chromophore when limited amounts are adsorbed; in aqueous solution association of water molecules must be preferred to hydrogen bonding to the chromophore.

Nature of Crosslinks

Since the crosslinks formed by photooxidation of polyvinyl alcohol can be broken down by treatment with dilute acid solution it is clear that carbon-carbon bonds such as might be formed by a process involving free radical intermediates are not involved.

The ease of dissolution in acid would be consistent with a mechanism involving salt formation between carboxyl groups in the polymer chain and chromic ions, but neither infrared spectra nor methylene blue tests provides any evidence for the formation of carboxyl groups.

It is known that cyclic ketals can be formed by reaction of carbonyl and hydroxyl groups[30] and it is possible that such a reaction could lead to crosslinking of the polyvinyl alcohol chains. However, there is no evidence of new absorption at frequencies expected for such structures in the infrared spectra, and it does not seem likely that such a structure could be hydrolyzed in decinormal acid.

The residual acetate groups in the polyvinyl alcohol do not affect the process; the material containing 1% acetate reacted similarly to that containing 20%.

The observation that crosslinking may be broken down or prevented by reagents (cyanide, ethylenediaminetetraacetic acid) which are known to form complexes with chromic ions suggests that formation of a coordination compound may be involved. There is no resemblance between the absorption spectrum of chromium (III) acetylacetonate and that of the exposed film; this renders it unlikely that complex formation by the β-diketone which would be formed by oxidation of two adjacent alcohol groups is the mechanism involved in the crosslinking. There is no evidence from the spectra for the presence of free β-diketone groups; the tendency to form unsaturated ketones greatly reduces the chance of β-diketone structures being formed. Similarly, the tendency to dehydration reduces the likelihood of β-hydroxy ketone groups being involved.

However, polyvinyl alcohol may be crosslinked by heating a film in which chromic chloride hexahydrate has been incorporated to a temperature high enough to drive off the water of crystallization. This experiment also suggests that groups formed by oxidation of the polyvinyl alcohol need not be involved in the crosslinking. The essential step is that coordinately unsaturated chromic ions should be formed. This may be achieved either by thermal dehydration or by photoreduction of acid chromate ions; the latter method allows the reaction to be used in a photographic process. Complexes with alcohols as ligands have not been much studied, but complexes of bivalent chromium of the type $[Cr(ROH)_6]^{++}$ have been reported,[31] the complex $[Ce(EtOH)(H_2O)_5]^{4+}$ has been identified as an intermediate in the oxidation of ethanol of ceric compounds,[32] and polyvinyl alcohol has been shown to form a complex $[Cu(RO)_2]^-$ with cupric ions.[33] Since the chromium-alcohol bond is, presumably, comparatively weak the alcohol groups can be replaced by groups (cyanide, ethylenediaminetetraacetic acid) capable of forming stronger bonds. The effect of dilute acid or alkali could be an example of acid-base catalysis of the aquation reaction of the complex, but analogous reactions do not seem to be subject to catalysis.[35] It may therefore be that the crosslinking involves catenation of the chromium in a binuclear complex.[36,37]

Thus the insolubilization and the photooxidation of the polyvinyl alcohol appear to be processes linked only by a common initial step—the photoreduction of the hydrogen chromate ion. A further process can occur at higher temperatures which renders the insolubilized film resistant to acids. This may be another independent process—the crystallization of the polymer.[34] It is intended to undertake further work to investigate this stage of the process.

References

1. Duncalf, B., *Graphic Technol.*, in press.
2. Duncalf, B., *Graphic Technol.*, in preparation.
3. Clarke, J. T., and E. R. Blout, *J. Polymer Sci.*, **1**, 419 (1946).
4. Flory, P. J., and F. S. Leutner, *J. Polymer Sci.*, **3**, 880 (1948); *ibid.*, **5**, 267 (1950).
5. Bosworth, P., C. R. Masson, H. W. Melville, and F. W. Peaker, *J. Polymer Sci.*, **9**, 565 (1952).
6. Matsumoto, M., and Y. Ohyanagi, *J. Polymer Sci.*, **46**, 520 (1960).
7. Davidson, G. F., *J. Textile Inst.*, **39**, T65 (1948).
8. Davies, W. G., and J. E. Prue, *Trans. Faraday Soc.*, **51**, 1045 (1955).
9. Neuss, J. D., and W. Rieman, *J. Am. Chem. Soc.*, **56**, 2238 (1934).
10. Bowen, E. J., and C. W. Bunn, *J. Chem. Soc.*, **1927**, 2353.
11. Bowen, E. J., T. A. Peacocke, and E. R. Wellburn, *J. Chem. Soc.*, **1931**, 1866.
12. Westheimer, F. H., *Chem. Revs.*, **45**, 419 (1949).
13. Leo, A., and F. H. Westheimer, *J. Am. Chem. Soc.*, **74**, 4383 (1952).
14. Cohen, M., and F. H. Westheimer, *J. Am. Chem. Soc.*, **74**, 4387 (1952).
15. Roček, J., and J. Krupička, *Collection Czech. Chem. Communs.*, **23**, 2068 (1958).
16. Graham, G. T. E., and F. H. Westheimer, *J. Am. Chem. Soc.*, **80**, 3030 (1958).
17. Brownell, R., A. Leo, Y. W. Chang, and F. H. Westheimer, *J. Am. Chem. Soc.*, **82**, 406 (1960).
18. Weber, K., and S. Ašperger, *J. Chem. Soc.*, **1948**, 2119.
19. Bowen, E. J., and J. E. Chatwin, *J. Chem. Soc.*, **1932**, 2081; also ref. 13.
20. Cartwright, H. M., *Process Engravers' Monthly*, **53**, 186 (1946).
21. Waters, W. A., *Quart. Rev.*, **12**, 277 (1958).
22. Matsumoto, M., K. Imai, and Y. Kazusa, *J. Polymer Sci.*, **28**, 426 (1958).
23. Lloyd, D. G., *J. Appl. Polymer Sci.*, **1**, 70 (1959).
24. Haas, H. C., H. Husek, and L. D. Taylor, *J. Polymer Sci.*, **A1**, 1215 (1963).
25. Braude, E. A., and E. R. H. Jones, *J. Chem. Soc.*, **1945**, 498.
26. Roberts, J. D., and C. Green, *J. Am. Chem. Soc.*, **68**, 214 (1946).
27. Evans, L. K., and A. E. Gillam, *J. Chem. Soc.*, **1941**, 815.
28. Hauser, K. W., R. Kuhn, A. Smakula, and M. Hoffer, *Z. Physik. Chem.*, **B29**, 363 (1935).
29. Evans, L. K., and A. E. Gillam, *J. Chem. Soc.*, **1945**, 432.
30. Rodd, E. H., Ed., *Chemistry of the Carbon Compounds*, Vol. IVb, Elsevier, Amsterdam 1959, p. 1526.
31. Schlafer, H. L., and H. Skoludek, *Z. Physik. Chem. (Frankfurt)*, **11**, 277 (1957).
32. Ardron, M., *J. Chem. Soc.*, **1957**, 1811.
33. Kuhn, W., and I. Toth, *Z. Naturforsch.*, **18A**, 112 (1963).
34. Sakurada, I., Y. Nukushina, and Y. Sone, *Ricerca Sci.*, **25A**, 715 (1955).
35. Stranks, D. R., in *Modern Co-ordination Chemistry*, J. Lewis and R. G. Wilkins, Eds., Interscience, New York–London, 1960, p. 115.
36. Grinberg, A. A., *An Introduction to the Chemistry of Complex Compounds*, Pergamon Press, London, 1962, p. 280.
37. Huckel, W., *Structural Chemistry of Inorganic Compounds*, Vol. I, Elsevier, Amsterdam, 1950, p. 154.

Résumé

On a étudié le phénomène de l'insolubilisation de l'alcool polyvinylique par le bichromate de potassium, par exposition à la lumière. La spectrométrie ultraviolette permet de montrer que les groupes hydroxyles secondaires sont oxydés en groupement cétoniques, mais l'insolubilisation doit être attribuée au pontage des chaines polymériques par la coordination des groupements alcooliques avec les ions chroniques naissants formés lors de la réduction du bichromate. Lorsqu'on expose les films d'alcool polyvinylique à une atmosphère saturée de vapeur d'eau, on élimine des spectres ultraviolets le maximum

d'absorption dû au groupement carbonyle, mais le spectre initial est restitué par chauf-
fage: ce phénomène est indépendant de la réaction de pontage.

Zusammenfassung

Das Unlöslichwerden von Polyvinylalkohol durch Kaliumbichromat unter Einwirkung
von Licht wurde untersucht. Mittels UV-Spektrometrie wurde festgestellt, dass sekun-
däre Hydroxylgruppen zu Ketogruppen oxydiert werden. Die Unlöslichkeit wird jedoch
auf Vernetzung der Polymerketten durch Koordination der Alkoholgruppen an "nas-
zente" Chrom(III)-Ionen, die durch Reduktion des Dichromats entstehen, zurückge-
führt. Bei der Einwirkung von wasserdampfgesättigter Luft verschwinden die Car-
bonyl-Absorptionsmaxima aus dem UV-Spektrum des Polyvinylalkoholfilms, doch kann
das ursprüngliche Spektrum durch Erhitzen wiederhergestellt werden. Diese Erschein-
ung ist von der Vernetzungsreaktion unabhängig.