

## Study of the Crosslinking of Polyvinyl Alcohol by Light-Sensitive Tetrazonium Salts

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### Synopsis

It has been reported that some diazonium compounds make polyvinyl alcohol insoluble to water under ultraviolet irradiation. We found that tetrazonium salts have even stronger light-hardening effects on polyvinyl alcohol than diazonium salts. We have studied by means of infrared spectra sensitive films consisting of polyvinyl alcohol and *o*-dianisidinetetrazonium chloride-zinc chloride double salts. After exposure of the film to ultraviolet rays, new absorption appeared at the 1250 and 1030  $\text{cm.}^{-1}$  bands; these absorptions were considered to be the asymmetric  $\nu(=\text{C}-\text{O}-\text{C})$  and the symmetric  $\nu(=\text{C}-\text{O}-\text{C})$ , respectively, in the infrared spectra. In ultraviolet spectra, new bands in the 260-270  $\text{m}\mu$  region appeared. Consequently it was concluded that the light-hardening effect of tetrazonium salts to polyvinyl alcohol was accomplished by a mechanism in which tetrazonium salts reacted with the OH groups of polyvinyl alcohol and crosslinked linear polyvinyl alcohol by phenyl ether bonds to form a network structure.

### I. INTRODUCTION

It is well known that most diazonium salts easily decompose and will release nitrogen gas by exposure to short wavelength light or heat.

It has been reported<sup>1,2</sup> that the films consisting of some diazonium salts and water-soluble high molecular weight compounds such as polyvinyl alcohol, gelatine, and carboxymethyl cellulose are sensitive to ultraviolet rays and become insoluble to water on ultraviolet irradiation, and that accordingly polyvinyl alcohol sensitized with some diazonium salts can be applied to the sensitive solutions for making plates for off-set printing. However, the mechanism of hardening of polyvinyl alcohol with diazonium salts is not completely clear.

It is the purpose of the present paper to study (1) the hardening effects on polyvinyl alcohol of diazonium and tetrazonium salts prepared from several amines and (2) the mechanism of the light-hardening effects in polyvinyl alcohol film containing *o*-dianisidinetetrazonium chloride-zinc chloride double salts. It was found that tetrazonium salts, having two diazonium groups in each molecule, hardened polyvinyl alcohol better than diazonium salts did.

Judging from these facts, it is proposed that the decomposition products of tetrazonium salts crosslink polyvinyl alcohol and make it insoluble to

water. But the hardening effects of diazonium salts are weak because they do not produce crosslinking. The infrared spectra show that the absorptions at  $3340\text{ cm.}^{-1}$  of the band assigned to  $\nu(\text{OH})$  of polyvinyl alcohol and the  $2240\text{ cm.}^{-1}$  band assigned to  $\nu(\text{N}\equiv\text{N})$  of diazonium groups decreased after exposure.

On the other hand, new absorptions appeared at  $1250$  and  $1030\text{ cm.}^{-1}$ , which are in the range of the absorptions by the asymmetric  $\nu(=\text{C}-\text{O}-\text{C})$  and the symmetric  $\nu(=\text{C}-\text{O}-\text{C})$ , respectively.

It is concluded that tetrazonium salts are decomposed by ultraviolet rays and form the bonds of a phenyl ether type with OH groups of polyvinyl alcohol.

In the ultraviolet spectra, a new peak appeared in the  $260\text{--}270\text{ m}\mu$  region after exposure. As it is reported<sup>3</sup> that phenyl ethers have the characteristic absorptions in the region of  $270\text{ m}\mu$ , the new peak might be ascribed to the formation of phenyl ether.

The cleavage of the ether bond is carried out with hydrogen halides (especially hydrogen iodide).<sup>4</sup> The light-hardened films of tetrazonium salts-polyvinyl alcohol are easily dissolved in aqueous solution of hydrogen iodide although these films are insoluble in boiling water.

According to these facts, it is presumable that the light-hardening effects resulting from the photochemical reactions between diazonium or tetrazonium salts and polyvinyl alcohol are based on the formation of phenyl ether type bonds and the tetrazonium salts give the strongly water-insoluble films because of the formation of crosslinking.

## II. EXPERIMENTAL

### Materials

**Polyvinyl Alcohol.** Polyvinyl alcohol (Nippon Gosei Chemical Co.), having an average degree of polymerization of 2000, and degree of saponification  $<99.5\%$  was used after further saponification and purification.

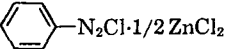
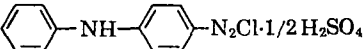
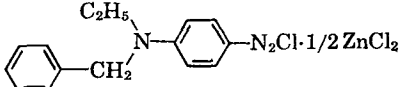
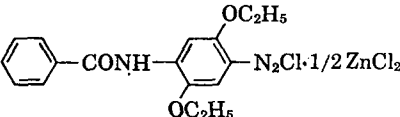
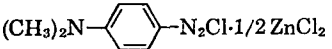
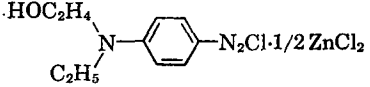
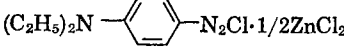
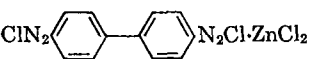
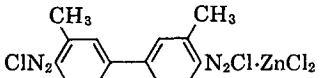
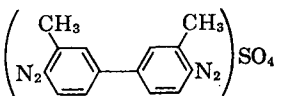
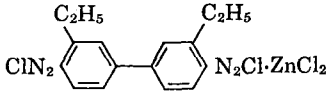
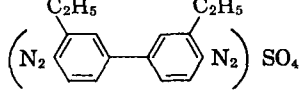
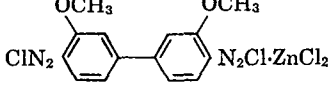
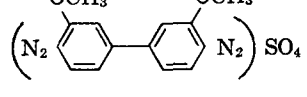
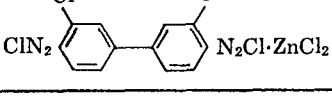
The saponification and purification were carried out by dissolving 2 g. of polyvinyl alcohol in 20 cc. of  $0.2N$  sodium hydroxide solution and keeping it at  $80^\circ\text{C}$ . for 1 hr. and precipitating polyvinyl alcohol from this solution by adding 200 cc. of methanol. The fibrous precipitate thus obtained was washed with clean methanol several times and dried in a desiccator.

**Diazonium and Tetrazonium Salts.** Diazonium and tetrazonium salts used are listed in Table I.

**Preparation of Benzene diazonium Chloride-Zinc Chloride Double Salts.** Aniline, 2 g., was dissolved in 20 cc. of  $10\%$  hydrochloric acid, and kept at  $0\text{--}5^\circ\text{C}$ . in an ice bath. To this solution, 3.5 g. of  $40\%$  aqueous solution of sodium nitrite was added, the temperature being kept at  $0\text{--}5^\circ\text{C}$ .

This mixture was allowed to react for 1 hr. with agitation and then filtered. To the filtrate, zinc chloride, 1.5 g., was added. The products were salted out with sodium chloride. The precipitate was filtered and washed

TABLE I. Diazonium and Tetrazonium Salts

No.	Salt	Formula	Light-hardening effect
1	Benzenediazonium chloride-zinc chloride double salts	 $\text{N}_2\text{Cl}\cdot 1/2 \text{ZnCl}_2$	Weak
2	Diphenylamine-4-diazonium sulfate-zinc chloride double salts	 $\text{N}_2\text{Cl}\cdot 1/2 \text{H}_2\text{SO}_4$	Weak
3	<i>p</i> -Ethylbenzylaminobenzenediazonium chloride-zinc chloride double salts	 $\text{N}_2\text{Cl}\cdot 1/2 \text{ZnCl}_2$	Weak
4	4-Benzoylamino-2,5-diethoxybenzene-1-diazonium chloride-zinc chloride double salts	 $\text{N}_2\text{Cl}\cdot 1/2 \text{ZnCl}_2$	Weak
5	<i>p</i> -Dimethylaminobenzediazonium chloride-zinc chloride double salts	 $\text{N}_2\text{Cl}\cdot 1/2 \text{ZnCl}_2$	Weak
6	<i>p</i> -Ethylethanolaminobenzene diazonium chloride-zinc chloride double salts	 $\text{N}_2\text{Cl}\cdot 1/2 \text{ZnCl}_2$	Weak
7	<i>p</i> -Diethylaminobenzediazonium chloride-zinc chloride double salts	 $\text{N}_2\text{Cl}\cdot 1/2 \text{ZnCl}_2$	Weak
8	Benzidinetetrazonium chloride-zinc chloride double salts	 $\text{N}_2\text{Cl}\cdot \text{ZnCl}_2$	Strong
9	<i>o</i> -Tolidinetetrazonium chloride-zinc chloride double salts	 $\text{N}_2\text{Cl}\cdot \text{ZnCl}_2$	Strong
10	<i>o</i> -Tolidinetetrazonium sulfate	 $\text{SO}_4$	Strong
11	Diethylbenzidinetetrazonium chloride-zinc chloride double salts	 $\text{N}_2\text{Cl}\cdot \text{ZnCl}_2$	Strong
12	Diethylbenzidinetetrazonium sulfate	 $\text{SO}_4$	Strong
13	<i>o</i> -Dianisidinetetrazonium chloride-zinc chloride double salts	 $\text{N}_2\text{Cl}\cdot \text{ZnCl}_2$	Strong
14	<i>o</i> -Dianisidinetetrazonium sulfate	 $\text{SO}_4$	Strong
15	Dichlorobenzidinetetrazonium chloride-zinc chloride double salts	 $\text{N}_2\text{Cl}\cdot \text{ZnCl}_2$	Strong

with aqueous saturated solution of sodium chloride and dried in a dark, cool place.

**Preparation of *o*-Dianisidinetetrazonium Chloride-Zinc Chloride Double Salts.** *o*-Dianisidine, 2 g., was dissolved in 16 cc. of 10% hydrochloric acid and kept at 0–5°C. in an ice bath. To this solution, 3.5 g. of 40% aqueous solution of sodium nitrite was added, the temperature being kept at 0–5°C. This mixture was allowed to react for 1 hr. with agitation and then filtered.

To the filtrate, zinc chloride, 1.5 g., was added. And the products were salted out with sodium chloride. The precipitate was filtered and washed with an aqueous saturated solution of sodium chloride and dried in a dark, cool place.

**Preparation of *o*-Dianisidinetetrazonium Sulfate.** *o*-Dianisidine 5 g., was dissolved in 70 cc. of dimethylformamide at room temperature and cooled to 0–5°C. in an ice bath. To this solution, 8 g. of concentrated sulfuric acid was added drop by drop, the temperature being kept at 0–5°C. To this mixture, 4 g. of amyl nitrite was added drop by drop also at 0–5°C.; then finally ethanol-ether (1:1) solution was added.

The precipitate was filtered and washed with the ethanol-ether solution several times and dried in a dark, cool place.

Preparation of other diazonium and tetrazonium salts follows the above mentioned methods. All the products were stored in a dark, cool place.

#### Light-Hardening Effects

The sensitive solutions used in testing the light hardening effects were prepared as follows: polyvinyl alcohol (5 wt. % aqueous solution), 10 g.,

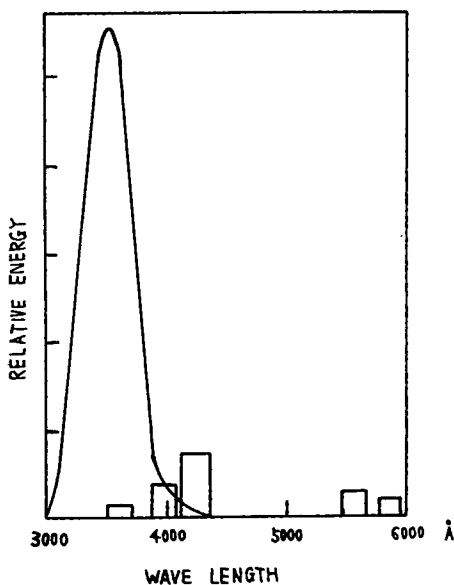


Figure 1.

diazonium or tetrazonium salts, 0.001 mole; distilled water, 10 cc. These solutions were coated on glass plate and dried at 30–40°C.

Then the plates were exposed to ultraviolet rays from a chemical lamp for 15 min. The spectral distribution curve of the lamp is shown in Figure 1.

After washing with water, the extent of the hardening effect was judged by dyeing the hardened layer on glass plates with methyl violet.

### Preparation of Sensitive Film

The sensitive films for the measurement of infrared spectra were prepared as follows.

The above solutions were coated on a piece of Bakelite plate having a smooth surface and dried at 40°C. in a dark place.

The dried film was stripped from the plate and set in the holder. The film used for the measurement of ultraviolet spectra was prepared in the same way, but in this case, the content of tetrazonium salts was 1 wt. %.

## III. RESULTS

### Light-Hardening of Polyvinyl Alcohol

As shown in Table I, the hardening effects of the diazonium salts (1–7) are weak, but tetrazonium salts (8–15) have the strong hardening effects and produce water-insoluble layers.

When diazonium compounds decompose, free radicals are produced.<sup>5</sup> It might be natural to presume that by the actions of these radicals, polyvinyl alcohol–diazonium or tetrazonium conjugation is formed. But the problem is whether the decomposition products of diazonium or tetrazonium salts combine with polyvinyl alcohol, or whether they transfer radicals to it and become stable themselves.

From the fact that tetrazonium salts which are able to produce two radicals in a molecule have a stronger hardening effects on polyvinyl alcohol than diazonium salts, it may be concluded that they form a network structure by crosslinking polyvinyl alcohol with the two radicals.

### Infrared Absorption Spectra

Infrared spectra are shown in Figures 2–4. In the absorption curve of polyvinyl alcohol which contains tetrazonium salts, the 3340  $\text{cm}^{-1}$  band assigned to  $\nu(\text{OH})$  decreases after exposure (Fig. 4). This shows that the tetrazonium salts reacted with OH groups of polyvinyl alcohol and the number of OH groups decreased.

As the 2920  $\text{cm}^{-1}$  band assigned to  $\nu(\text{CH})$  and the 1140 and 850  $\text{cm}^{-1}$  band assigned to  $\nu(\text{C—C})$  do not decrease, and the absorptions attributed to  $\nu(\text{C=O})$  of carbonyl groups do not appear, oxidation or splitting of polyvinyl alcohol does not seem to occur. The absorptions at 2240  $\text{cm}^{-1}$  assigned to  $\nu(\text{N}\equiv\text{N})$  and at 1595  $\text{cm}^{-1}$  which might be due to  $\nu(\text{C—N})$  conjugated with the ring decrease because of decomposition of diazonium

groups by light. The absorption at  $1575\text{ cm.}^{-1}$  by phenyl groups which is intensified by the polar radicals, decreases with the decrease of the polar radicals.

On the other hand, new absorptions appeared at  $1250$ ,  $1180$ , and  $1030\text{ cm.}^{-1}$ .

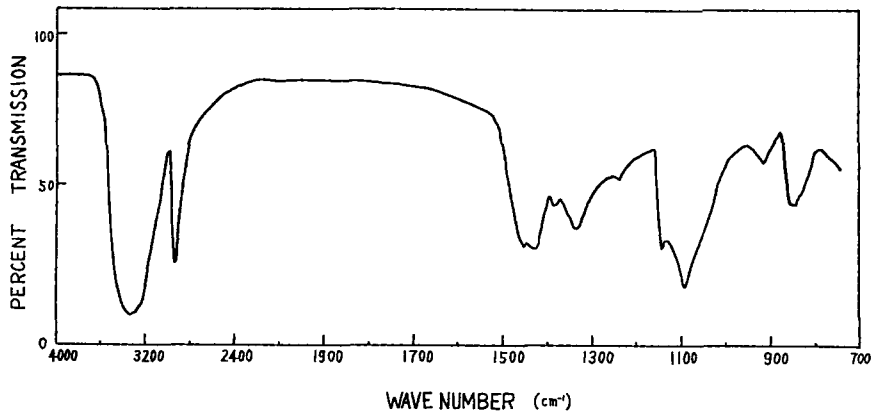


Fig. 2. Infrared spectrum of polyvinyl-alcohol film (film thickness is  $10\mu$ ). A Nippon Bunko Model IR-S spectrophotometer was used.

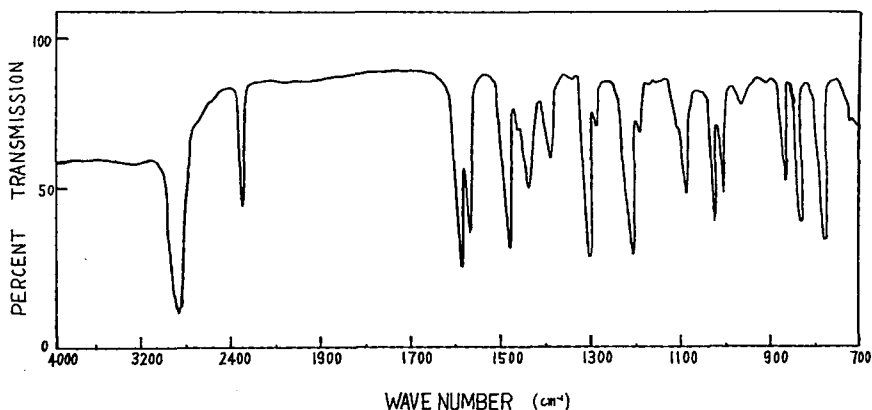


Fig. 3. Infrared spectrum of *o*-dianisidinetetrazonium chloride-zinc chloride double salts (nujol, NaCl cell).

The  $1250\text{ cm.}^{-1}$  band might be attributed to  $\nu(\text{C—O})$  of phenol compound, or asymmetric  $\nu(=\text{C—O—C})$  of a phenyl ether compound. If this band is due to  $\nu(\text{C—O})$  of a phenol compound, its  $\nu(\text{OH})$  also will appear. But there is no absorption by  $\nu(\text{OH})$ , or  $\delta(\text{OH})$  of phenol compound, and so the  $1250\text{ cm.}^{-1}$  absorption is attributed to asymmetric  $\nu(=\text{C—O—C})$  of phenyl ether. The bands at  $1030$  and  $1180\text{ cm.}^{-1}$  are due to symmetric  $\nu(=\text{C—O—C})$  and  $\nu(\text{C—O})$ , respectively. The absorptions and assignments are summarized in Table II.

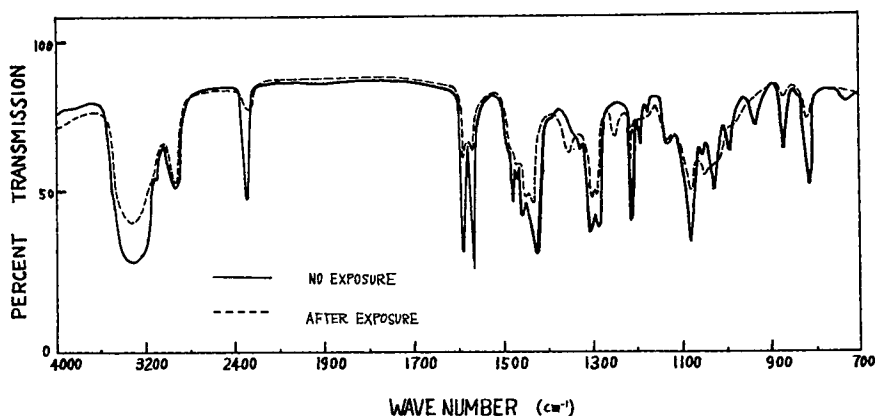


Fig. 4. Infrared spectra of polyvinyl alcohol film containing *o*-dianisidinetetrazonium chloride-zinc chloride double salts.

It is proposed that tetrazonium salts are decomposed by light and react with OH groups of polyvinyl alcohol by free radical reactions and crosslink it.

TABLE II  
Infrared Absorption and Band Assignment for Polyvinyl Alcohol Film Containing *o*-Dianisidinetetrazonium Chloride-Zinc Chloride Double Salts and Exposed to Ultraviolet Irradiation

Wave number, cm. <sup>-1</sup>	Change after exposure	Assignment <sup>a</sup>
3340	Decrease	$\nu(\text{OH})$ of polyvinyl alcohol
3080	Decrease	$\nu(\text{CH})$ of phenyl
2240	Decrease	$\nu(\text{N}\equiv\text{N})$
1595	Decrease	$\nu(\text{C}-\text{N})$
1575	Decrease	Phenyl group
1475, 1430, 1405	Decrease	$\delta(\text{CH})$ of $-\text{OCH}_3$
1315	New appearance	$\nu(\text{C}-\text{O})$ of phenyl ether
1265	Decrease	$\delta(\text{CH})$
1250	New appearance	Asymmetric $\nu(=\text{C}-\text{O}-\text{C})$ of phenyl ether
1210	Decrease	$\delta(\text{CH})$
1180	New appearance	$\nu(\text{C}-\text{O})$ of phenyl ether
1030	New appearance	Symmetric $\nu(=\text{C}-\text{O}-\text{C})$ of phenyl ether
925, 830, 810	Decrease	$\delta(\text{CH})$

<sup>a</sup>  $\nu$  = stretching vibration;  $\delta$  = bending vibration.

### Ultraviolet Spectra

Ultraviolet spectra of polyvinyl alcohol films containing tetrazonium salts (Figs. 5-7) show that after exposure to ultraviolet rays, absorptions over  $300 \text{ m}\mu$  disappear and new bands appear at  $270 \text{ m}\mu$ . This is regarded

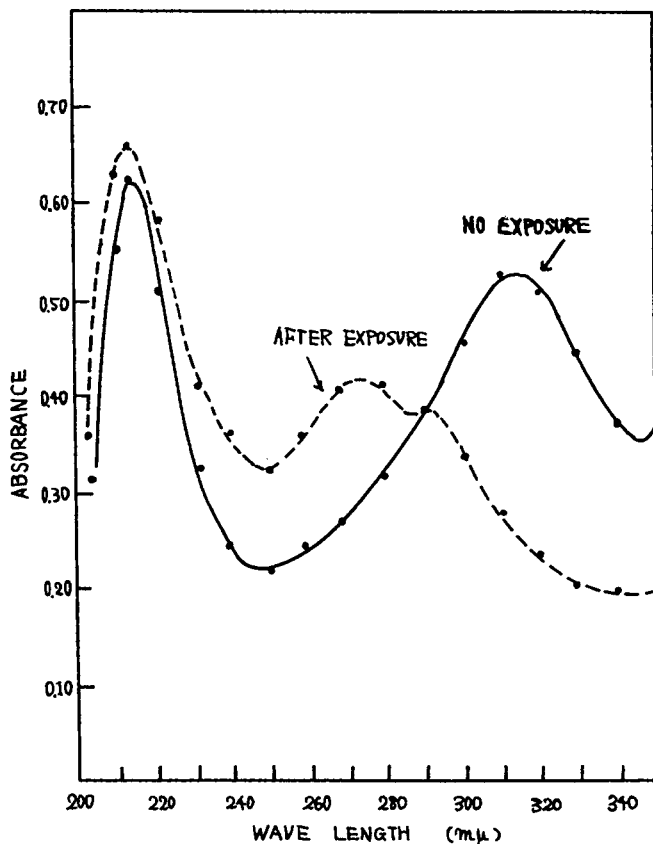
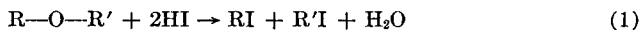


Fig. 5. Ultraviolet spectra of polyvinyl alcohol film containing *o*-dianisidinetetrazonium chloride-zinc chloride double salts.

as evidence for the formation of phenyl ether, because ethers have characteristic peaks at 270  $m\mu$ . For example, anisole has its peak at 270  $m\mu$ . Polyvinyl alcohol films containing tetrazonium salts and exposed to ultraviolet rays are insoluble in boiling water.

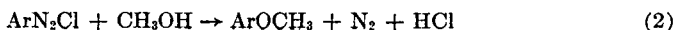
If polyvinyl alcohol is combined with the decomposition products of tetrazonium salts by ether bonds and so it is insoluble to water, the light-hardened films will become water-soluble if the ether bonds are split, as for example, by hydrogen iodide.<sup>4</sup>



It was found that the light-hardened films dissolved in an aqueous solution of hydrogen iodide at 80°C.

#### IV. DISCUSSION

When diazonium salts are decomposed in alcohol by light or heat, phenyl ethers are produced.<sup>3</sup>





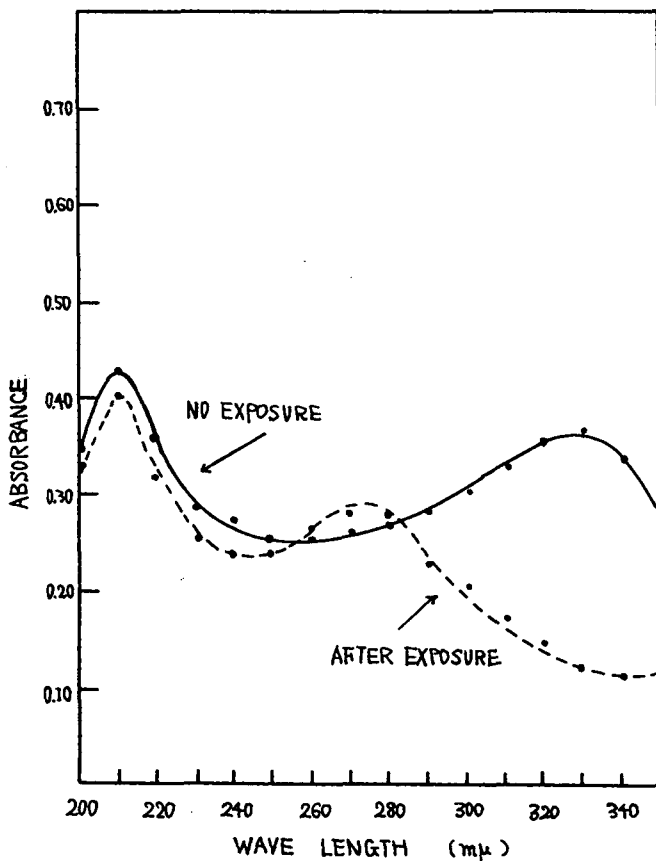
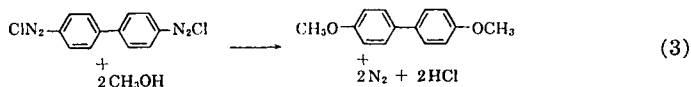


Fig. 6. Ultraviolet spectra of polyvinyl alcohol film containing benzidinetetrazonium chloride-zinc chloride double salts.

Similar reactions might be possible between tetrazonium salts and methanol:



The infrared spectra of reaction products of benzidinetetrazonium chloride with methanol are shown in Figure 8.

The absorption band which appears at  $1250\text{ cm.}^{-1}$  is attributed to asymmetric  $\nu(\text{=C-O-C})$  of phenyl ether.

When diazonium or tetrazonium salts are decomposed thermally or photochemically, free radicals are produced.<sup>5</sup> These free radicals might react with OH groups of polyvinyl alcohol and result in the formation of ether bonds.

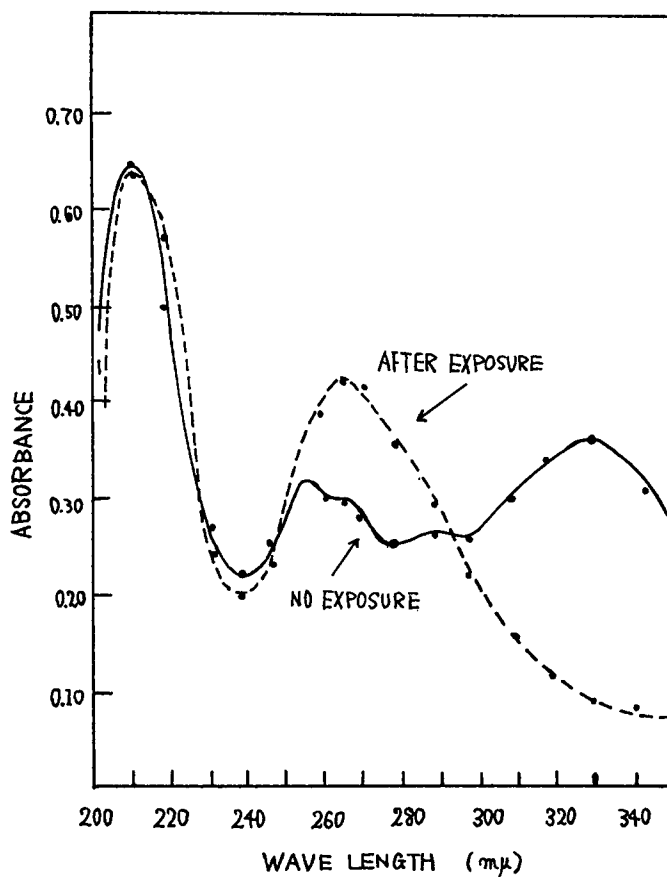


Fig. 7. Ultraviolet spectra of polyvinyl alcohol film containing diethylbenzidinetetrazonium sulfate.

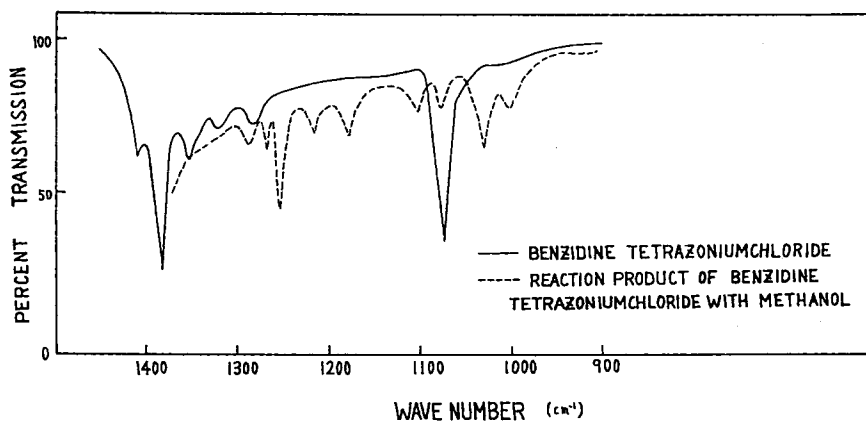
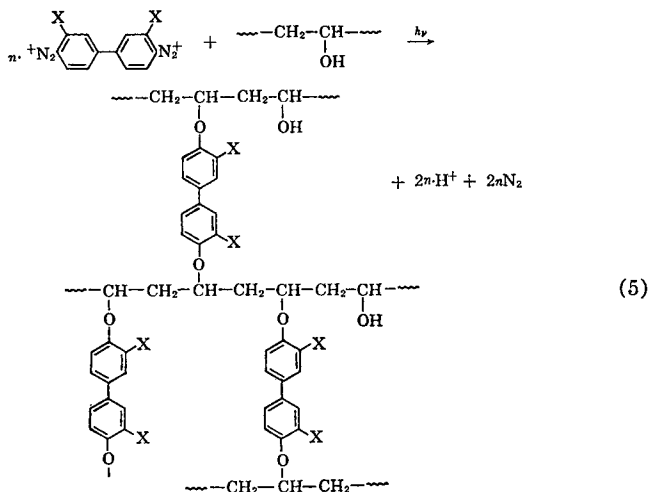
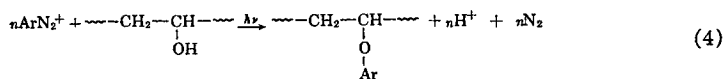


Fig. 8. Infrared spectra of benzidinetetrazonium chloride and products of thermal decomposition in methanol.

A proposed mechanism is given in eqs. (4) and (5).



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### Résumé

Selon des travaux antérieurs certains composés de diazonium rendent l'alcool polyvinylique insoluble dans l'eau après irradiation par les rayons ultraviolets. Nous avons trouvés que les sels de tétrazonium ont un effet de durcissement à la lumière plus marqué que les sels de diazonium. Nous avons étudié le spectre infrarouge de la pellicule sensible constitué d'alcool polyvinylique et de sels doubles de chlorure de zinc et de chlorure de tétrazonium de l'*o*-dianisidine. Quand on expose cette pellicule aux rayons ultraviolets des nouvelles régions d'absorption apparaissent à  $1250\text{ cm}^{-1}$  et  $1030\text{ cm}^{-1}$ . On considère que les bandes sont l'asymétrique  $\nu(\text{=C---O---C})$  et la bande symétrique  $\nu(\text{=C---O---C})$  dans l'infrarouge. Dans l'ultraviolet on voit des nouvelles bandes à  $260\text{--}270\text{ m}\mu$ . Par conséquent on peut conclure que l'effet de durcissement à la lumière des sels de tétrazonium avec l'alcool polyvinylique s'effectue d'une manière tel que les sels de tétrazonium réagissent avec les groupes OH de l'alcool polyvinylique et ont ponté l'alcool polyvinylique linéaire par des liens éther-phénylé pour former une structure réticulée.

### Zusammenfassung

Wie aus früheren Arbeiten anderer Autoren hervorgeht, bewirken gewisse Diazoniumsalze eine Unlöslichkeit von Polyvinylalkohol in Wasser nach der UV-Bestrahlung. Bei

Tetrazoniumsalzen wurde ein stärkerer Lichthärtungseffekt als bei Diazoniumsalzen beobachtet und durch Aufnahme von IR-Spektren des aus Polyvinylalkohol und *o*-dianisidintetrazoniumchlorid-Zinkchlorid-Doppelsalzen bestehenden Filmes untersucht. Nach der UV-Bestrahlung des Filmes traten im IR-Spektrum neue Banden bei 1250  $\text{cm}^{-1}$  und 1030  $\text{cm}^{-1}$  auf, die dem asymmetrischen  $\nu(=\text{C}-\text{O}-\text{C})$  bzw. dem symmetrischen  $\nu(=\text{C}-\text{O}-\text{C})$  zugeordnet wurden. Ausserdem traten im UV-Spektrum neue Banden im Bereich von 260–270  $\text{m}\mu$  auf. Aus diesen Befunden schliesst man, dass die Lichthärtungswirkung von Tetrazoniumsalzen auf Polyvinylalkohol nach folgendem Mechanismus verläuft: Das Tetrazoniumsalz reagiert mit den OH-Gruppen des Polyvinylalkohols und vernetzt den linearen Polyvinylalkohol durch Phenylätherbindungen unter Bildung einer Netzwerkstruktur.

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