CHEMISTRY LETTERS, pp. 727-730, 1977. Published by the Chemical Society of Japan

A DIFFUSION OF METAL INTO POLYMERIC LAYER BY A NOVEL ELECTRO-INDUCED METALLOCHROMIC REACTION

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A copper evaporated organic film consisting of a poly(vinyl-chloride) matrix and a precursor of a chelating agent was tinged with magenta (λ_{max} = 520 nm) under successive treatments of electron bombardment and heating. On the bombarded part, structure of film was changed from laminated double layers to single organic one. The coloration was due to formation of a cupric metallochrome (colored chelate) and was closely related to the change of chemical property of evaporated copper by the above treatments. Thus the copper disappearance from the surface was estimated to have occurred by diffusion into the organic layer.

Diffusion of metal into organic layer occurred under successive treatments of electron bombardment and heating. In a laminated specimen consisting of a thin evaporated copper film and a poly(vinyl-chloride) (PVC) matrix layer containing a photo- or thermo-chromic benzospiran derivative (1', 3'-dihydro-1', 3', 3'-trimethyl-6-nitro-8-methoxyspiro[2H-1-benzopyran-2,2'-[2H]indole] : SP), the copper disappeared from the surface and the polymeric layer was tinged with magenta (λ_{max}= 520 nm) by successive treatments of electron bombardment (9~17 kV) and heating (over the T_g point of matrix). The coloration of the organic layer was localized at the bombarded area and closely related to the disappearance of the surface copper.

A magenta product appeared both in a solution and in a polymeric layer. In a tetrahydrofuran (THF) solution containing SP, cupric acetylacetonate ($Cu[acac]_2$) and hydrogen chloride (HCl), a metastable magenta product (λ_{max}= 510 nm) was formed by irradiation of UV rays.1) In a poly(vinyl-butyral) matrix containing SP and cupric chloride ($CuCl_2$), a similar magenta product (λ_{max}= 520 nm) was also formed by electron bombardment and heating. The product prepared in the polymer was stable in contrast with that in the THF solution. These products were prepared from a reaction between cupric ions and open-ring species of SP (SP') formed photochemically or thermally. In a molecule of the product, a bonding ratio of SP' to cupric ion (SP'/Cu^{++}) was estimated to be equal to 2. It was stabilized by HCl as a result of formation of chloride salt and was thought to be a salt type colored cupric chelate (METALLOCHROME, $[Cu\cdot(SP')_2\cdot Cl_2]$). In a PVC matix containing SP and $Co[acac]_2$, HCl was liberated from the matrix by electron bombardment and a cobaltous metallochrome as same as the cupric one was formed selectively at the bombarded part.2)

This paper deals with the disappearing process of surface copper on the laminated specimen. The study is mainly discussed with regard to change in the absorption spectrum of an organic layer and detection of the residual surface copper. In a specimen, the organic layer consisting of PVC polymer (PVC; Mitsubishi-Montsant Co. #4005, T_g= 80°C or a copolymer of PVC and poly(vinyl-acetate) (PVC·PVAc); Sekisui Chem. Co. #Eslec-C, T_g= 80°C) and SP (synthesized by Nihon Kanko Shikiso Kenkyujo Ltd., m.p.= 163°C). It was coated on a transparent Nesa glass (thickness about 3 µm). The copper film was evaporated on the organic layer by vacuum evaporation at a pressure of 10^{-5}torr (thickness; several tens angstrom). The specimen was bombarded by a medium-energy electron (9~17 kV) in vacuo and next was heated (100~160°C) on a hot-plate in open air. the absorption spectrum of the specimen was measured as that of the organic layer after the surface copper was removed off with an aqueous solution of ferric chloride. The change of surface copper was checked by a deposition of nickel by electrodeless plating. The procedure of plating was as follows; the surface copper of specimen was activated with a hydrochloric solution of palladium chloride and next was soaked in a plating solution of nickel (Japan Kanigen Co. #Blue-Sumar)

The specimen changed the color of its organic layer as well as its surface under the treatment. By bombardment, the surface copper did not change but the organic layer was tinged with yellow. By post-heating, the surface copper of the bombarded area disappeared and the color of the organic layer turned magenta (λ_{max}= 520 nm). While the surface copper of the non-bombarded area looked slightly frosty due to oxidation, the organic layer was tinged pale blue (λ_{max}= 600 nm) by formation of SP' which was due to thermal reaction. Figure 1 shows a picture of the specimen after treatment. The eight squares were the bombarded areas and were colored magenta. The rest was covered by residual copper. Figure 2 shows the absorption spectra of specimens at various temperatures of post-heating. The spectrum of bombarded area was altered by the temperature of post-heating. In the spectrum, absorption peaks at 130°C were located at 560 and 600 nm. They were blue-shifted by post-heating at higher temperatures and in the case at 150°C, a single peak was located at 520 nm. But the spectrum at 160°C was fairly different from the others. Over the T_g point of matrix, the temperature rising would act to decrease the viscosity of the matrix, so spectrum changes due to formation of the colored product were more drastic at high temperatures. But at temperature of 160°C, almost the melting point of SP where its volatility increased, the product density fell down. The same tendency in color change appeared as an effect of heating time. In a short-time heating, the absorption peak located at 560 nm and it blue-shifted with eleongation of the heating time. As a result, the optimum heating conditions showing the absorption peak of organic layer at 520 nm was estimated to be a heating temperature of 150°C and a heating time of 5 min. for both matrices.

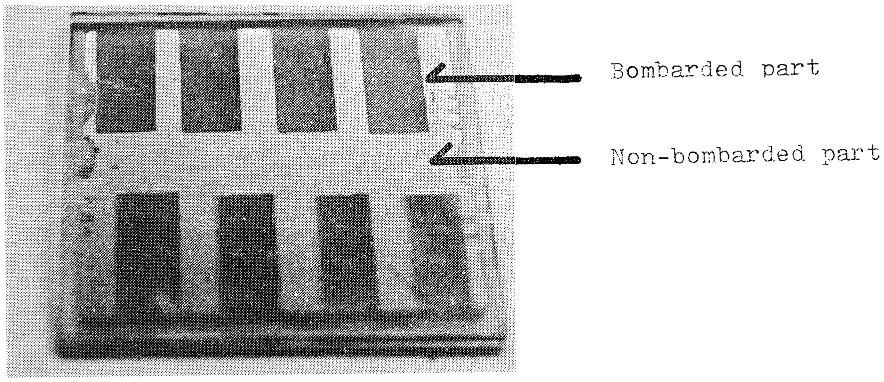


Figure 1. Picture of specimen after both treatments.

The bombarded electron penetrates a specimen and loses its energy. The effects of bombardment are discussed with regard to two parameters; the one is the number of electrons supplied to the specimen, and the other is its energy expressed by an accelerating voltage. The energy of each bombarding electron is far greater than that required for ordinary chemical reactions. Therefore on the bombardment, the difference between the accelerating voltage of 9 kV and that of 17 kV is rather negrigible. And the number of bombarding electrons expressed by a charge density (coulomb [= sample current x time] /cm^2 : C/cm^2) has important meaning for the energy supplied to the specimen. The accelerating voltage of each electron influences its penetrating depth and is related closely to a reaction range in the specimen.

Figure 3 shows relations between absorbance of bombarded specimens at 520 nm and a charge density of the bombardment at three accelerating voltages. The coloration appeared at the charge density of 10^{-7}C/cm^2 in order of magnitude. The absorbance grew with the increase of charge density, until it attained a peak at about 8 x 10^{-7}C/cm^2 and the specimen was tinged with yellow. The turning point was affected by the accelerating voltage. The main effect of accelerating voltage appeared on the depth of reaction range in the specimen. In the case of 13 kV, the penetration depth of electron was estimated to be comparable to the thickness of specimen (3 μm) and the reaction range would spread through the whole specimen. In the case of 9 kV, the electron reached half way through the thickness. The density of the product was thinner than that of 13 kV, so that the absorbance curve was located at a lower level. Although in the case of 17 kV, the penetrated electron passed through the specimen so that it did not supply its entire energy to the specimen. Thus the absorbance level was located lower than that of 13 kV. Surface copper was so thin, the energy loss due to passing through it was negligible.$^{3)}$

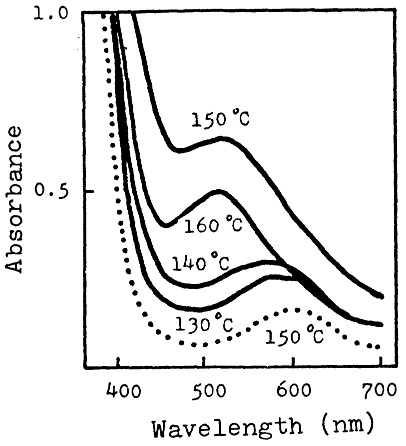


Figure 2. Absorption spectra of specimens at various temperatures of post-heating.

—— : Bombarded specimen
..... : Non-bombarded one
Specimen : surface copper— 50 Å
organic layer; matrix—PVC, SP—15wt%, 3 μm
Bombardment : 17 kV—6 x 10^{-7} C/cm^2
Heating time : 5 min.

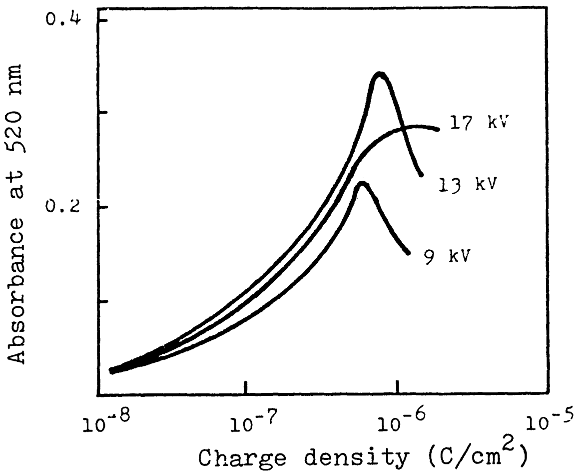
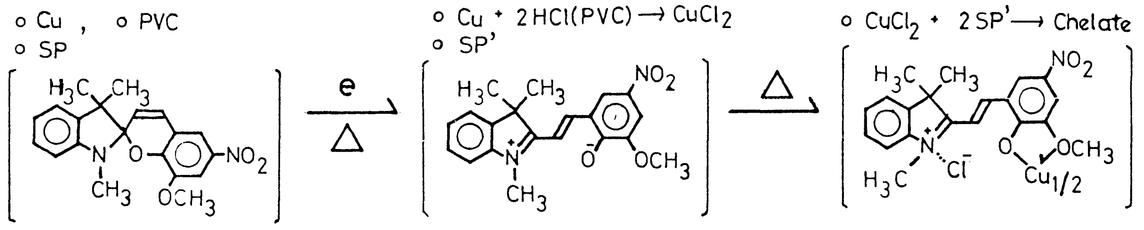


Figure 3. Relations between absorbance and charge density of the bombardment at various accelerating voltages.

Specimen : surface copper—40 Å
organic layer; matrix—PVC·PVAc, SP—10 wt%, 3 μm.
Heating : 150°C—5 min.

The change of evaporated copper due to the treatments was checked by nickel-plating. On the non-bombarded specimen, nickel was deposited on the surface copper layer. On the bombarded one, it appeared that the deposition occurred depending on the color of organic layer. When the absorption peak of the spectrum was located at 520 nm, nickel was not generally deposited on the surface. But its peak was located at 560 nm, nickel appeared distinctly. It meant the existence of surface copper while formation of colored product showing an absorption peak at 520 nm was closely related to the disappearance of surface copper. The maximum thickness of surface copper layer which can be removed by the treatments was estimated to be 40 Å and as such was not affected by the accelerating voltage of bombarding electrons. The charge density required for the removal was concerned to the SP content of organic layer. In the series of specimen consisting of the surface copper having a thickness of 40 Å and an organic layer containing PVC·PVAc matrix having SP content of 7 to 15 wt%, the minimum charge density of the disappearance varied from 8×10^{-8}C/cm^2 for 7 wt% to 4×10^{-7}C/cm^2 for 15 wt%. Moreover in a dissolved solution of treated organic layer, the copper was detected quantatively by the atomic absorption analysis.

Materials composing the specimen were affected remarkably by the treatments. Under bombardment, a PVC molecule is degradated and HCl is liberated. Finally its molecular chains are cross-linked with each other. By post-heating, SP is turned to SP' with a chelating function, and surface copper is converted to $CuCl_2$ at the boundary of both layers by the liberated HCl. The colored product in the specimen showed the same spectrum as the cupric metallochrome in poly(vinyl-butyral) matrix but did not appear with other benzospiran derivative having no chelating function. Thus the colored product showing its absorption peak at 520 nm would be the same as the above mentioned cupric metallochrome and the reaction scheme of it supposed to be shown as follows;



As a result, the disappearance of evaporated copper would be due to a diffusion of it into the organic layer. The diffusing depth of copper into the organic layer is a so complicated problem, although it may be connected with the penetration depth of electrons. Further study is being continued to clarify the diffusing mechanism and its depth.

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(Received March 30, 1977)