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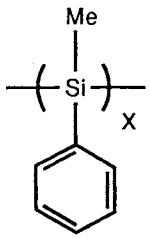
Image Formation Due to Thermo-chemical Decoloration in Blue Colored Organopolysilane/Titanylphthalocyanine Layered Film Patterned by Ultra-violet Light

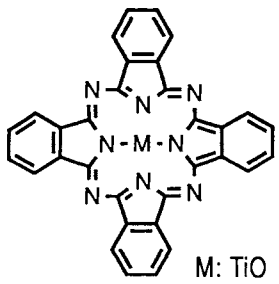
Mikio KAKUI, Kenji YOKOYAMA, and Masaaki YOKOYAMA*
Chemical Process Engineering, Faculty of Engineering, Osaka University,
Yamadaoka, Suita, Osaka 565

Blue colored poly(methylphenylsilane) (PhMeSi)x/titanylphthalocyanine (TiOPc) layered films have been found to suffer thermo-chemical decoloration effectively by ultra-violet (UV) light irradiation followed by heat treatment at temperature of 250 ℃. The decoloration has been confirmed to result from chemical destruction of TiOPc, which is initiated by thermo-decomposition of organopolysilane, and particularly accelerated by UV irradiation. The present thermo-chemical decoloration can be applicable as a new image recording.

Organopolysilanes having σ-conjugated Si sequence in the backbone chain show several marked physical and chemical properties different from the carbon-based polymers, and have recently attracted much attention from their potential technological utilization.[1] In their physical properties, organopolysilanes are characterized with their high hole drift mobility as much as 10^{-4} $cm^2V^{-1}s^{-1}$ [2-4] and have been extensively investigated for their application as a new class of charge carrier transporting polymeric materials for photoreceptors of electrophotography.[5-7] On the other hand, organopolysilanes have been also studied for lithographic application based on their well-known chemical properties that they easily undergo photodegradation and photo-oxidation during irradiation of UV light in air.[8] In our previous work, we reported an organic layered photoreceptor using an organopolysilane, typically poly(methylphenylsilane) (PhMeSi)x, as a hole transport layer combined with titanylphthalocyanine (TiOPc) pigment as a charge photogenerator,[6] and furthermore successfully demonstrated that the layered photoreceptor turned to a memory photoreceptor by imaging with UV light irradiation, which enable xerographic multiduplication without every light exposure, for an example combining the unique physical and chemical properties of organopolysilanes.[9] During these studies, quite accidentally, we have found that the (PhMeSi)x/TiOPc layered films suffered decoloration of TiOPc blue color effectively by heating only in the UV irradiated portion, resulting in a pattern formation corresponding to the UV image with good contrast. In the present letter, we would like to report the details of the new observation of thermo-chemical decoloration in the layered films, which can be applicable as a new image recording.



Poly(methylphenylsilane)
(PhMeSi)x



Titanylphthalocyanine
(TiOPc)

In Fig. 1 is demonstrated a typical example of the pattern formation due to thermo-chemical decoloration in the layered film. The pattern formation process is illustrated in Fig. 2. Firstly, the (PhMeSi)x/TiOPc layered films used

here consisted of a (PhMeSi)x layer of about 3 μm thick on the top of a thin TiOPc pigment under-layer (thickness < 1 μm) on aluminum or glass substrate, which was prepared by spin-coat technique from a slurry of TiOPc dispersed in polyvinylbutyral (PVB) resin with 1:1 by weight or by vacuum deposition of the pigment. The molecular weight of (PhMeSi)x used was >5000 as measured by GPC using polystyrene for calibration. Next, the layered film was exposed to UV light (300-400 nm) through a photomask as shown in Fig. 2(2). In the UV exposed area, photodegradation of (PhMeSi)x, which is accompanied with reactive intermediate products by Si-Si bond scission followed by the formation of Si-O bond in air, proceeds easily from surface to bulk of the over-coated (PhMeSi)x film by well-known spectral self-bleaching effect.[8] At this stage, no color change was observed, but when the sample was heated at about 250 ℃ as shown in Fig.2(3), the decoloration occurred very rapidly within few seconds only in UV exposed area of the film, i.e., the UV pre-exposed area of the film was discolored, while the unexposed area remained unaltered. Thus, the positive image pattern shown in Fig. 1 was obtained by this process, which is characterized by high contrast, high resolution and effective tone reproduction. Figure 3 shows the absorbance changes at 690 nm, which are attributed to TiOPc absorption, in the UV pre-exposed layered films as a function of the heat treated temperature until 300 ℃. A_{690}(25 ℃) and A_{690} indicate the optical absorbance at 690 nm before and after heating at a given temperature for 5 min, respectively, and hence A_{690}/A_{690}(25 ℃) represents the contrast ratio of decoloration in the (PhMeSi)x/TiOPc layered films. The increasing of absorption in an unexposed film near 250 ℃ is probably due to a morphological transformation of TiOPc. The onset temperature of discoloring of the layered films tends to reduce with increasing UV pre-exposure. Consequently, the heat treatment at about 250 ℃ gives rise to high contrast between UV exposed and unexposed areas. By heating over 250 ℃, however, the discoloring occurred regardless of UV pre-

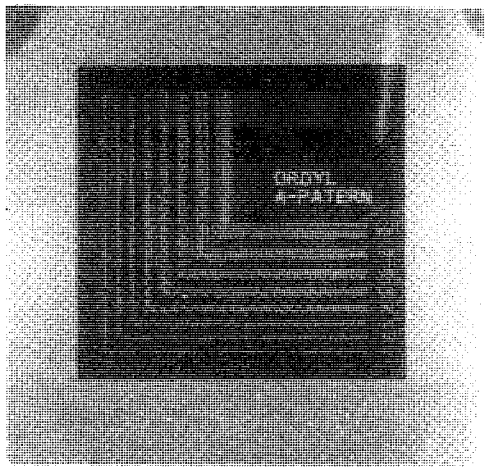


Fig. 1. A typical example for thermo-chemical decoloration in a (PhMeSi)x/TiOPc layered film. White area corresponds to discolored area contrasted with blue colored background (dark area in the photograph).

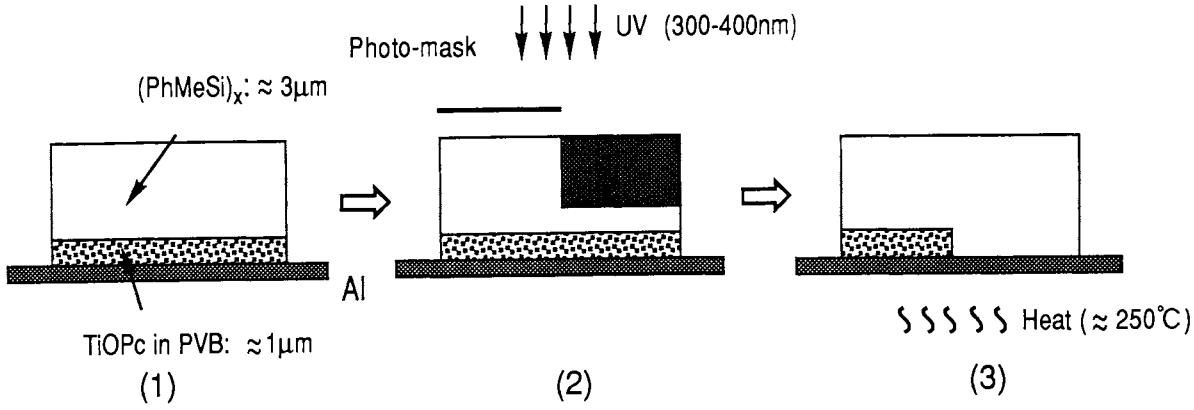


Fig. 2. Thermo-chemical decoloration process: (1) Structure of a (PhMeSi)x/TiOPc layered film, (2) Imaging process; photodegradation of (PhMeSi)x by UV light, (3) Thermo-developing; discoloring only in the UV pre-irradiated area.

exposure. It should be noted that interestingly, this phenomenon was observed only in the films incorporating (PhMeSi)x and TiOPc or VOPc (vanadylphthalocyanine), but not observed in some combinations of other phthalocyanines such as metal-free, copper and zinc phthalocyanines. Figure 4 shows reflectance spectra of UV exposed layered films before and after the heat-treatment. Owing to Al substrate as underlying reflector, the reflectance at 830 nm, which corresponds to an emitting band of a typical laser diode, drastically changed from 5% to 70%. This result strongly indicates a possible application of the (PhMeSi)x/TiOPc layered films to a new type of optical-recording media utilizing their optical property changes due to thermo-chemical decoloration. Analytical studies on the mechanism of the present thermo-chemical decoloration are now in progress, but some preliminary results are described here. The similar phenomenon, a significant absorbance decrease, has been found in a toluene suspension of TiOPc containing (PhMeSi)x when UV light was merely irradiated at room temperature. In the absence of (PhMeSi)x, as a matter of fact, it was not observed. When 60-fold excess of methanol was added in the suspension as an efficient chemical trap for the radicals, the discoloring of TiOPc was effectively depressed. These results suggest that the thermo-chemical decoloration in (PhMeSi)x/TiOPc layered film is based on chemical processes, which may involve the destruction of TiOPc ring initiated by reactive intermediate species (e.g., silylenes and silyl radicals) formed in the thermolysis of organopolysilanes. The ESR analysis during the thermolysis of organopolysilanes also provided a significant information. In the UV irradiated (PhMeSi)x film, a distinct ESR signal which is ascribed to the silyl radical species (g = 2.004) was observed from temperatures as low as 200 ℃, while in the unirradiated film no signals were observed up to 280 ℃. This result indicates that the UV exposure to (PhMeSi)x caused an acceleration of the thermolysis of (PhMeSi)x and therefore, the acceleration depending on UV exposure as shown in Fig. 3 accounts for the appearance of tone reproduction in the present thermo-chemical image formation. The chemical products due to the decoloration,

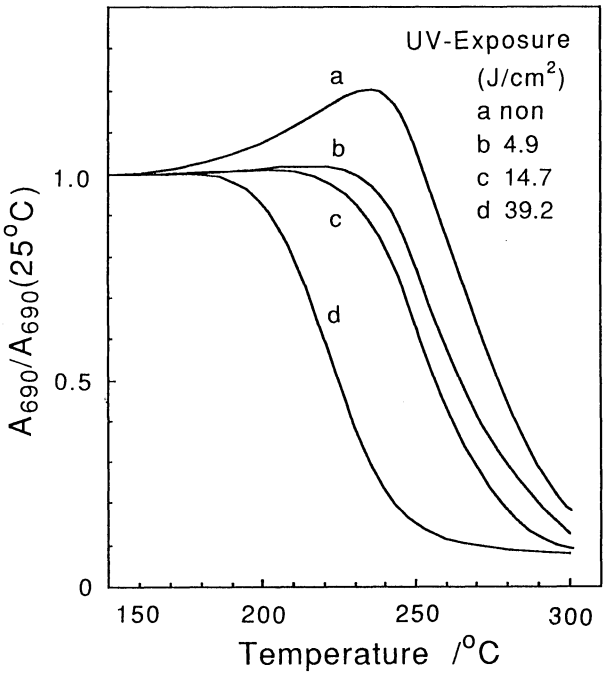


Fig. 3. Absorbance changes in UV preexposed (PhMeSi)x/TiOPc layered films due to heat-treatment at various temperature.

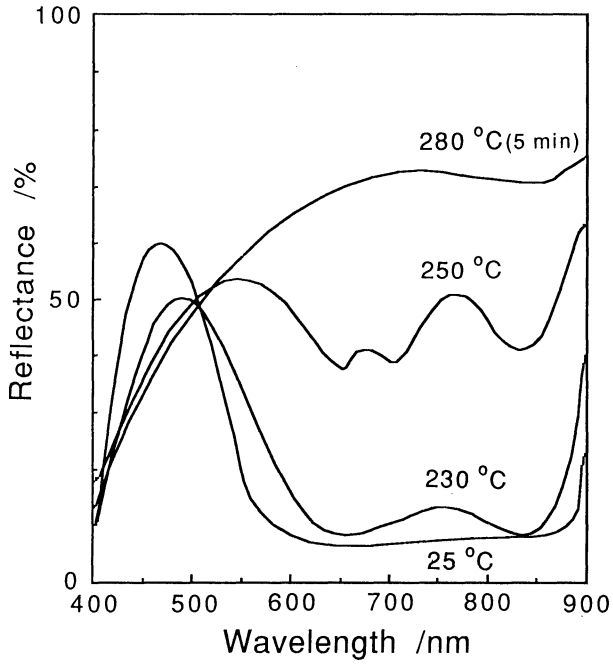


Fig. 4. Reflection spectra changes in the UV exposed layered film due to heat-treatment.

which is colored like gold with a weak absorption in visible region as shown in Fig. 4, were analyzed by FT-IR.[10] Absorption bands attributed to interaction of TiOPc and (PhMeSi)x were not observed in the layered film after simply UV exposed. In the discolored layered film, however, the absorption bands of TiOPc disappeared and a new absorption peaked at 920 cm^{-1} was observed evidently, which can be assigned to Si-O-Ti stretching vibrational mode. The formation of Si-O-Ti bonds in the discolored film was also suggested by the results of XPS analysis, in which a high energy shift of 2 eV was observed in Ti_{2p} core level after decoloration.

In summary, we have newly found that the UV irradiated (PhMeSi)x/TiOPc film suffer efficient decoloration by heating at 250 ℃, which is attributed to the chemical destruction of TiOPc initiated by thermo-decomposed species of organopolysilanes and demonstrated the thermo-chemical image formation as their application. The results described here seem to indicate a possible application to a new type optical-recording media.

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