Why Does a Color-Developing Phenomenon Occur on Thermal Paper Comprising of a Fluoran Dye and a Color Developer Molecule?

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The mechanism of the color development on thermal paper, comprising a fluoran dye (S-205) and a color developer molecule, such as bisphenol A, was elucidated based on spectroscopic analyses (IR, and NMR) on an isolated black-colored compound prepared by a reaction of S-205 and bisphenol A. We propose that this black-colored compound is, indeed, a color-developing complex (**CDC**) with a definite molar ratio (S-205 : bisphenol A = 1 : 4) which has been formed between the open-form S-205 (generated by the cleavage of the lactone ring of S-205: zwitterion) and bisphenol A through hydrogen-bonding. The enthalpy gain associated with the formation of **CDC** plays an important role for black-color formation on thermal paper.

Thermal paper is presently widely used in our daily life because of the easiness of printing that requires simple hardware for quick printing, which can make printing devices compact and practically maintenance-free. Thermal paper[1] is composed of a supporting material (paper) and a coating layer in which a fluoran dye precursor, a color developer, and a sensitizer are dispersed uniformly as fine particles. When a certain surface area on thermal paper is heated by the thermal head of the printer, the fluoran dye precursor, the color developer, and the sensitizer melt together and form a color as the result of a chemical reaction. Among many fluoran dyes, 2′-anilino-6′-(*N*-ethyl-*N*-isopentyl) amino)-3′-methylspiro[isobenzofuran-1(3*H*), 9′-(9*H*)xanthen]-3-one, hereafter referred to as **S-205**, is widely used as a dye precursor for black color development; the black color is due to the strong absorption maxima of this dye in the visible region at around 450 (yellow) and 590 nm (purple), which are in a relation of complementary colors.

A simple acid-base equilibrium mechanism[2] for color developing has been proposed and accepted without any definite experimental evidence until now. That is, a proton released from phenols attacks an ester oxygen atom in the fluoran dye (S-205, for example), which leads to a cleavage of the lactone-ring, as shown in Scheme 1. By opening the lactone ring, the electronic state of spiro-carbon in S-205 changes from sp^3 hybridization to sp^2, and π-electron conjugation in the xanthene ring extends over to give rise to a black-color formation. Although it is experimentally sure that black-color development of the dye occurs by the addition of strong acids, such as HCl and CH_3COOH, a question prevails as to whether the same mechanism works between dyes and phenols, because; (1) the acidity of phenols is known to be weak (pK_a is 8–11)[3], (2) carboxy functional group generated in the dye as a result of the cleavage of the lactone-ring takes the carboxylate form ($–COO^-$), not the carboxylic acid form (–COOH), which was elucidated from IR spectrum measurements (see Results and Discussion), and (3) the above color-developing reaction proceeds more in solvents with less polarity than in high polarity. We, in this paper, propose an alternate, or co-working, mechanism for color developing phenomena on thermal paper, between a fluoran dye and phenols, represented here by bisphenol A.

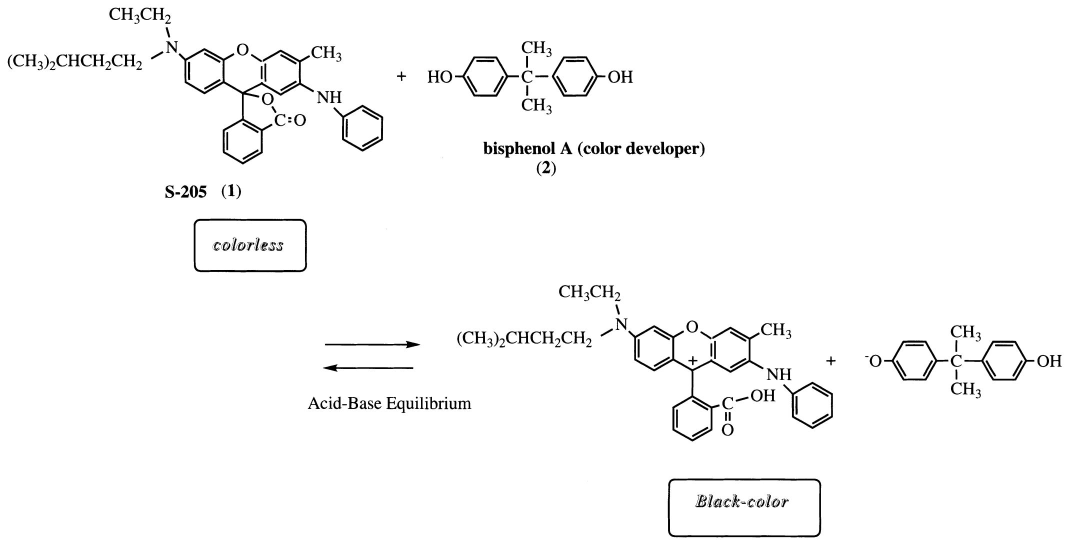
The new mechanism is based on our findings that a black-colored compound between S-205 and bisphenol A can be isolated under certain experimental conditions. This compound was characterized to be a molecular complex (**C**olor **D**eveloping **C**omplex, **CDC**) consisting a definite molecular ratio of the dye and the color developer. We deduce that **CDC** is stabilized by the hydrogen bonding interaction between the dye and the color developer.

Results and Discussion

Preparation and Isolation of the Color Developing Complex (CDC). The color developing complex (**CDC**) was prepared as black precipitates by dissolving both S-205 and color developer bisphenol A in hot toluene, and rapidly cooling down the toluene solution in an ice bath. Slow cooling-down and prolonged cooling precipitated solely bisphenol A crystals and obscured the molar ratio of the two components in the prepared **CDC**. The obtained black precipitates were quickly filtered and washed by cold toluene with suction, and then dried in vacuo to give rise to a black powder. This black powder is fairly stable as long as it is in the solid state. However, its black color disappears soon when it contacts with oil and various organic solvents.

Infrared (IR) Spectrum of CDC. The frequencies of the characteristic C=O stretching vibration peaks of the **CDC** and relevant compounds are summarized in Table 1, and their IR spectra are shown in Fig. 1. The IR spectrum of the **CDC** indi-

Uncertain Reaction Mechanism for Color-developing on the Thermal Paper



Scheme 1.

Table 1. Infrared Spectra in the Region of the C=O Stretching Vibrations of S-205 + Bisphenol A Coler Developing Complex: **CDC** and Its Relevant Molecules

Compound	Wavenumber / cm^{-1}	Measurement condition
(S-205+Bisphenol A) **CDC**	1639 (anti-symmetric) 1362 (symmetric)	KBr disc
S-205	1751	KBr disc
Lactone ring opened S-205	1759	in CCl_4

cates that the proposed acid-base equilibrium mechanism for color developing (Scheme 1) can not be justified. An IR spectrum of the lactone form S-205 in KBr disc showed a characteristic C=O stretching vibration inherent to a lactone functional group at 1751 cm^{-1}. However, carbonyl vibration of the black-colored **CDC** appeared at 1639 cm^{-1}. This wavenumber is rather low to be assigned as a C=O stretching vibration mode in the –COOH group. The standard IR spectrum data book[4] has reported that the C=O vibration of aromatic carboxylic acids (Ar–COOH) appears at around 1680–1700 cm^{-1}, while characteristic vibration modes inherent to carboxylate –COO$^-$ appear at 1610–1550 cm^{-1} (anti-symmetric mode carbonyl vibration of COO$^-$) and 1420–1300 cm^{-1} (symmetric mode of COO$^-$). The IR spectrum of the **CDC** also showed a symmetric mode carbonyl vibration at 1362 cm^{-1}. A lower wavenumber shift (100 cm^{-1}) and the emergence of symmetric mode –COO$^-$ vibration of the **CDC** indicate the existence of a carboxylate functional group (–COO$^-$) in the **CDC** instead of a carboxyl group (–COOH). In order to make sure that S-205 in the **CDC** really exists a zwitterion, the IR spectrum of the open-form S-205, as shown in Scheme 1 (which can be generated by the reaction with HCl to lead the cleavage of the lactone ring) was measured in CCl_4. In the IR spectrum of this open-form S-205, a carbonyl C=O stretching vibration appeared at 1759 cm^{-1}, which can be assigned to the COOH group. Though both compounds (**CDC** and open-form S-205 in the strong acid) showed a black color, the IR spectra of these compounds indicate that they exist as different chemical species; i.e. the **CDC** exists as a zwitterion, and the open-form S-205 generated by the reaction with strong acids exists as a lactone ring-opened carboxylic acid, as shown in Scheme 1, which is in good agreement with a previous report by Nakatsu's group.[5] The principal factor to stabilize the **CDC** can be attributed to hydrogen bonding between S-205 and bisphenol A. The hydroxy group in bisphenol A works as a hydrogen-bond donor to form a hydrogen bond with electron-rich hydrogen-bond acceptor atoms in the zwitterionic form of S-205.

Chemical Properties of the CDC. This isolated black-colored **CDC** is a thermodynamically metastable compound. For instance, it gradually degrades to the starting materials (S-205) and color developer bisphenol A when heated, particularly under high humidity (i.e. black-color compound turns to colorless one). The degradation was confirmed by detecting the formation of bisphenol A crystals from the **CDC** after the treatment. In addition, **CDC**s are found to be dissolved in many hydrogen-bond forming solvents, such as alcohols, dimethyl sulfoxide, and acetone, to give a colorless solution, which indicates the complete dissociation of the **CDC** to the

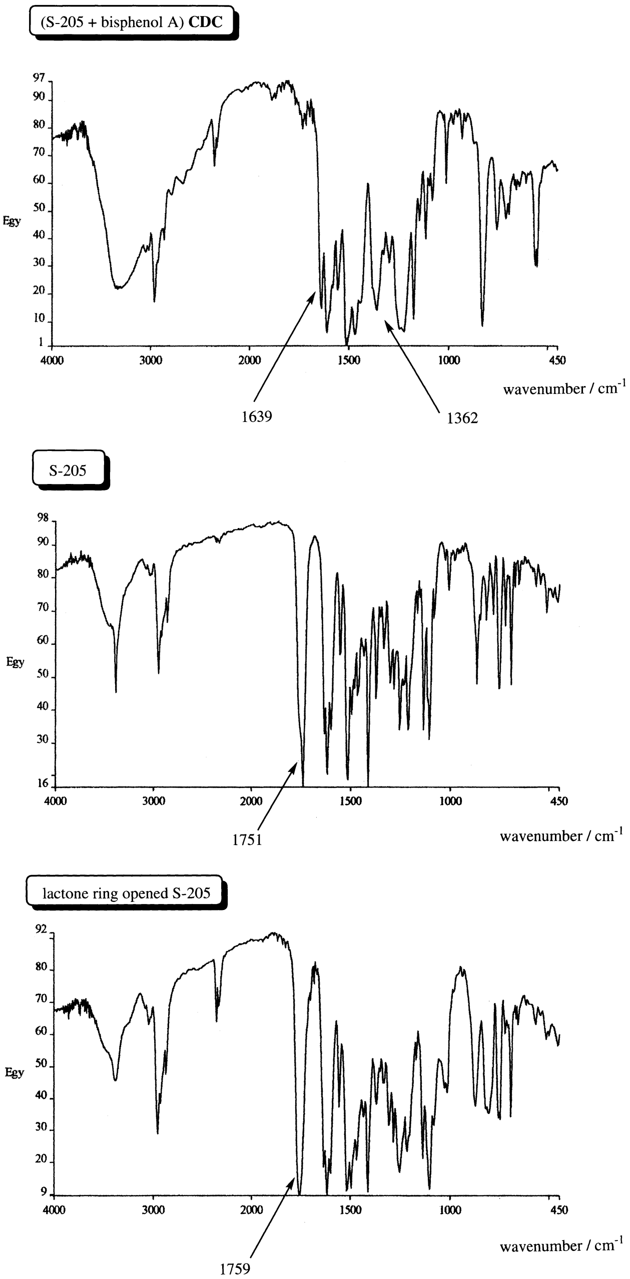


Fig. 1. IR spectra of the S-205 + bisphenol A Color Developing Complex (**CDC**) and its relevant molecules.

consisting dye and phenols. Due to this metastablity of the **CDC**, experiments in the liquid phase do not lead to the inherent character of the **CDC**. However, both HPLC analyses (column; LiChrospher 100RP18e, eluate; $CH_3CN:H_2O$:phosphoric acid) and ^{1}H-NMR measurements of the **CDC** solution have determined that the molar ratio of the **CDC** has a constant value of S-205:bisphenol A = 1:4, regardless of the composition of the starting materials in hot toluene (S205:bisphenol A was altered from 1:1 to 1:6), as shown in Fig. 2. This result strongly suggests that S-205 and color developer bisphenol A interact to form a well-fixed complex as a black solid.[6]

^{13}C-NMR Spectra of S-205 and the CDC. Although the **CDC** dissociates into its component molecules in organic solvents, it was found that this phenomenon takes time in such solvents as $CDCl_3$, a solvent with a certain polarity to dissolve the **CDC**, yet having a less hydrogen bond-forming nature.

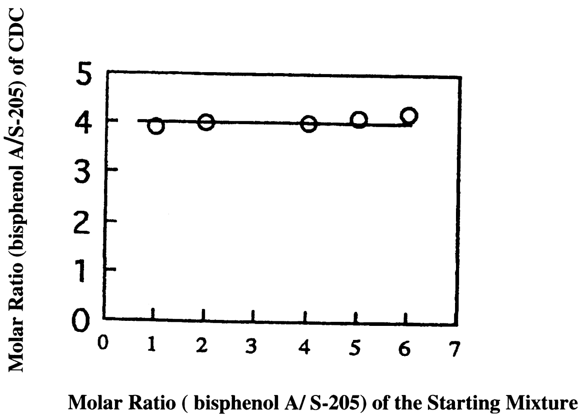


Fig. 2. Molar ratio of **CDC** (S-205:bisphenol A) determined ^{1}H-NMR measurements by changing the composition of the starting mixture (S-205:bisphenol A = 1:1 – 1:6).

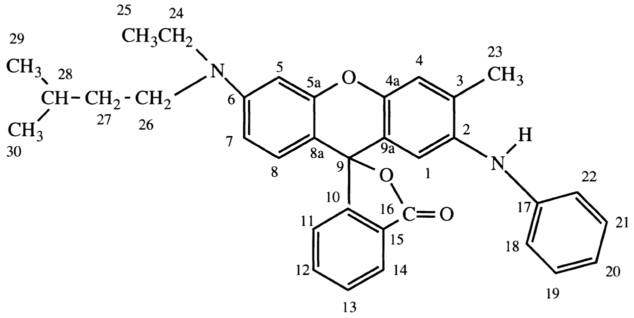
By taking advantage of this slow process of dissociation, we could obtain some structural information of **CDC** from the ^{13}C-NMR spectrum immediately after preparing a sample solution by comparing with that of the ring-closed (lactone) form of S-205. The ^{13}C-NMR spectrum data of the lactone form S-205 are summarized in Table 2.

We found that a peak corresponding to the spirocarbon (C9), which would drastically change its atom configuration during the course of color development, showed both broadening and a considerable decrease in the intensity of **CDC**. Similar phenomena were observed for the C5, C6, C7 and C8 atoms, that were thought to bear a partial charge appearing on the spirocarbon in the colored form. Peak broadening and a reduction of the intensity in smaller magnitude were also observed for the alkylamino carbons at the C6 position. It should be noted here that other carbons did not experience these peak changes, even immediately after sample preparation. Both the broadening and peak reduction phenomena disappeared after several hours to give identical peaks to the lactone form of S-205 (and bisphenol A). The broadening of the ^{13}C-NMR peaks and the decrease in the signal intensity on some specified carbon atoms in S-205 can be attributed to an inter-molecular interaction between S-205 and bisphenol A. The inter-molecular interaction may restrict the molecular motion at the interactive-sites. As a result of the restriction of molecular motion at specific carbon atoms, the effective correlation times at these carbon atoms (τ_c) would be longer. Because the signal line-width ($\Delta\nu_{1/2}$), relaxation time (T_1), and effective correlation time (τ_c) are correlated with each other, as shown in Eq. 1,[7] we can recognize a restriction of molecular motion (i.e. the longer effective correlation time) would lead to a broadening of the peak and a decrease of the signal intensities,

$$\Delta\nu_{1/2} \approx 1 / T_1 = h^2 \gamma_C^2 \gamma_H^2 r_{CH}^{-6} N \tau_c \ , \qquad (1)$$

where γ_C and γ_H are the gyromagnetic ratios of the carbon and hydrogen atoms, respectively. r_{CH} is the interatomic distance between the C and H atoms. N is the number of directly adja-

Table 2. The ^{13}C-NMR Spectral Peaks' Assignment of S-205 Measured in $CDCl_3$



Chemical shift / ppm	Assignment	Chemical shift / ppm	Assignment
12.10	C25	119.48	C1
17.88	C23	123.88	C11
22.46	C29, C30	124.38	C14
25.68	C28	126.09	C10
35.60	C27	128.80	C8
44.30	C24	128.97	C19, C21
47.95	C26	129.90	C13
84.43	C9	134.82	C5a
96.80	C5	136.75	C4a
103.97	C8a	145.12	C3
108.35	C7	146.41	C15
114.67	C22, C18	149.27	C6
116.85	C9a	152.34	C17
118.37	C4	152.38	C2
118.58	C20	168.73	C16

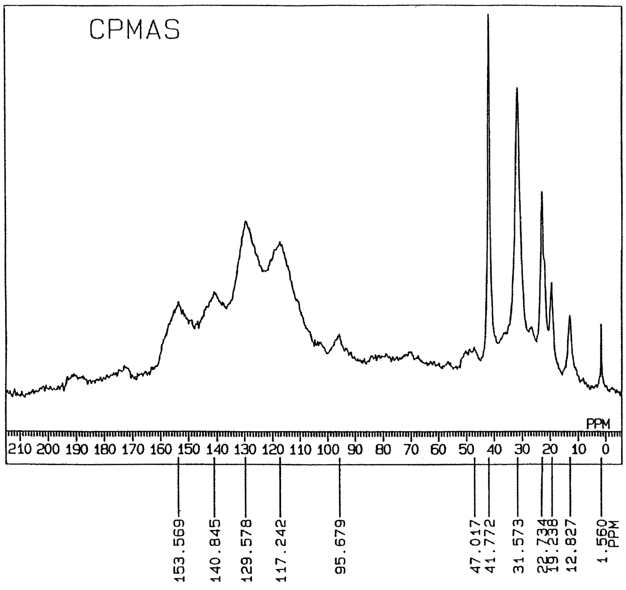


Fig. 3. CP/MAS ^{13}C-NMR spectrum of S-205 + Bisphenol A Color Developing Complex (**CDC**).

cent protons.

This interesting behavior of the ^{13}C-NMR spectrum in an inert solvent, such as $CDCl_3$, was not observed in polar protic and aprotic solvents. In the case where a noticeable solvent–solute(**CDC**) interaction can be expected, the **CDC** may dissociate quickly and only show the spectra of the superposition of S-205 and bisphenol A.

Solid State ^{13}C-NMR Spectrum of CDC. The solid state ^{13}C-NMR spectrum was measured using the CP/MAS technique to obtain structural information inherent to the solid **CDC**. The spectrum is shown in Fig. 3. In addition to broadening of the signals on the whole, a noticeable feature specific to the solid state ^{13}C-NMR spectrum is the disappearance of the spiro-carbon atom signal (C9 carbon), whose peak was found at around 84 ppm of the lactone form S-205 in solution or in the solid state. A dipolar dephasing CP/MAS technique was applied to enhance the signal of the C9 carbon, which enabled us to locate it at around 133 ppm. The chemical-shift value of 133 ppm is consistent with the idea that the carbon atom is in the sp^2 hybridized state.

The Other Attempts for Spectral Analyses. Other attempts, including (1) ^{1}H-NMR measurements of **CDC** in solution, (2) UV-vis spectrum analyses of **CDC** in solution, and (3) FAB (Fast Atom Bombardment) Mass measurement of **CDC** in a more hydrophobic *m*-nitrobenzyl alcohol matrix, turned out to be unsuccessful in terms of obtaining additional structural information inherent to **CDC**. In all of the above cases, solutions and matrices became colorless before and during the measurements, suggesting the spontaneous dissociation of **CDC** to its component molecules. All experimental results in solution and with FAB Mass measurements proved the fragile character of **CDC**, which, together with the color reduction phenomenon of **CDC** at elevated temperatures, particularly under high humidity, agrees very well with the color unstability observed on thermal paper (thermal paper was notorious for its low image persistence). A clue concerning with the chemical species of a black-color image developed on thermal paper was obtained from reflection UV-vis measurements of **CDC**. The reflection UV-vis spectrum of a black-color image (**CDC**) on S-205 + bisphenol A thermal paper (Fig. 4) showed absorption maxima at λ_{max} = 468 nm and 580 nm. These two absorption peaks were essentially the same as those in the spectrum of the solution of S-205 in 2,2,2-trifluoroethanol (Fig. 5). In the latter case, the color formation was assigned to be a zwitterionic form of S-205[8,9] stabilized by an ample amount of

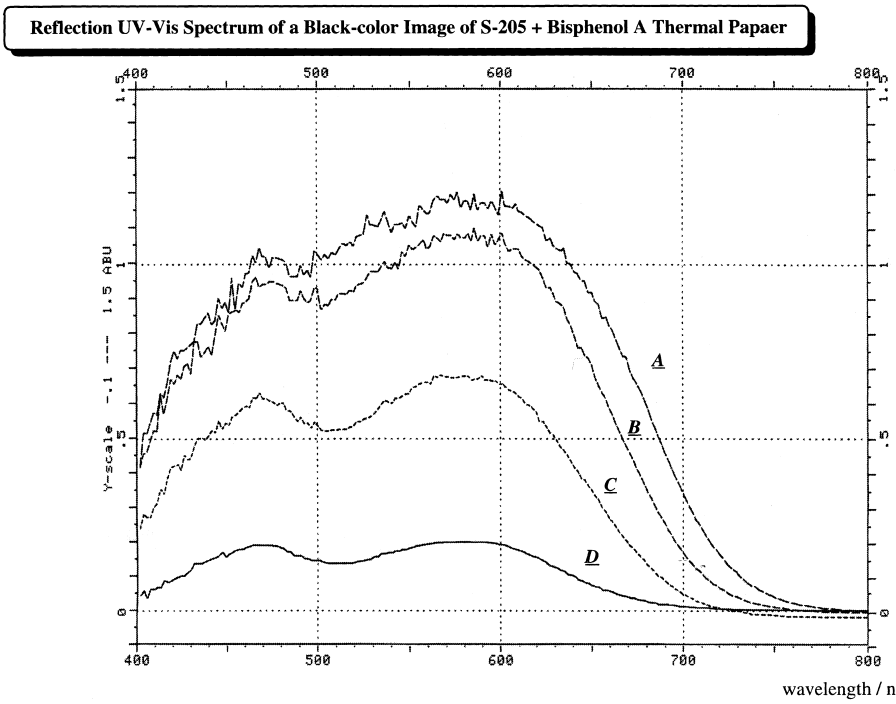


Fig. 4. Reflection UV-vis spectrum of black-color image developed on a thermal paper composed of S-205 and bisphenol A. Magnitude of black-color developing was dependent on added thermal energy on a printer head. Added energy (mW) for each scan (A, B, C, D) was 10, 6, 5, 4 mW, respectively.

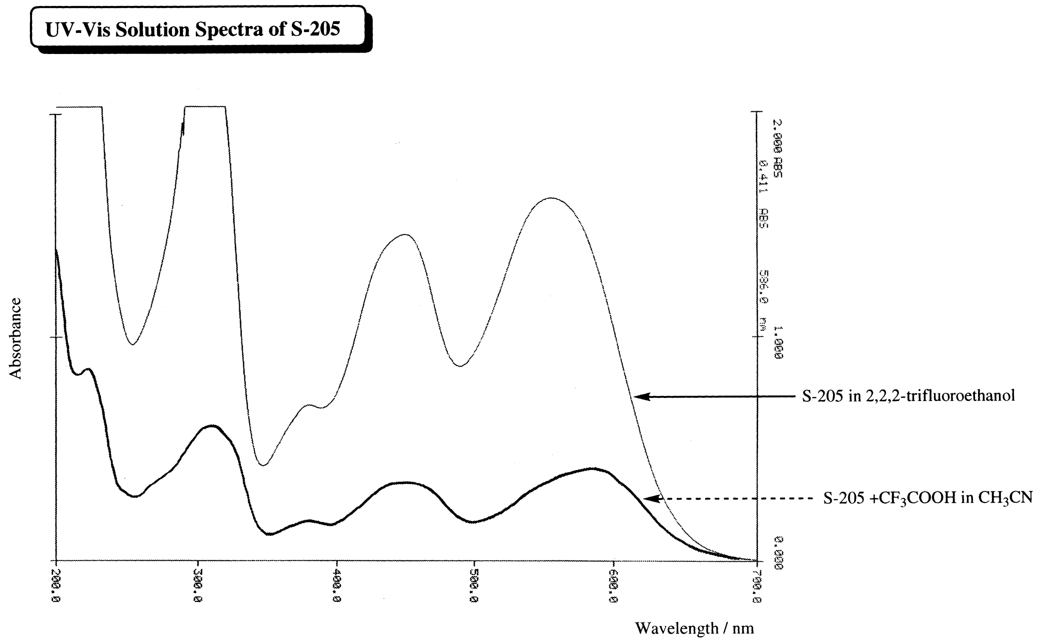
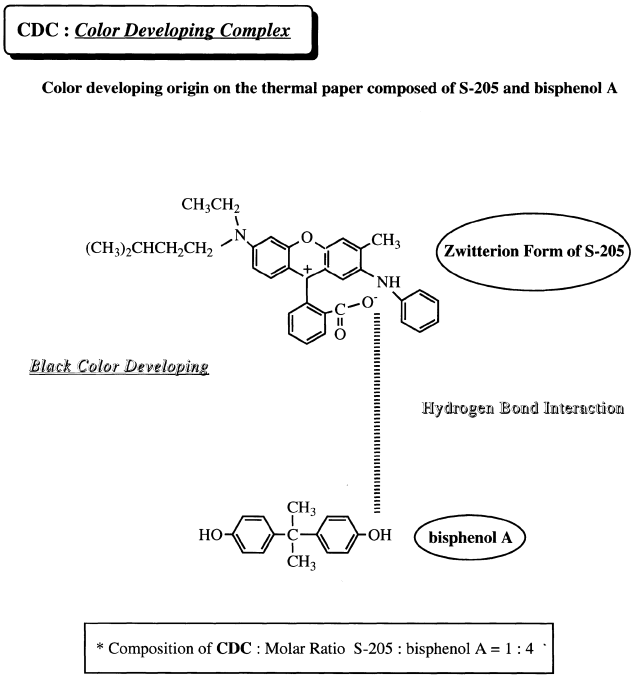


Fig. 5. UV-vis solution spectra of S-205 (4.15×10^{-5} mol dm^{-3}) in 2,2,2-trifluoroethanol and S-205 (1.71×10^{-5} mol dm^{-3}) + trifluoroacetic acid (1.20×10^{-3} mol dm^{-3}) in CH_3CN.

2,2,2-trifluoroethanol surrounding S-205. This spectral agreement strongly suggests that a basic chromophore responsible for the color formation in solutions and in the solid state is the same, and is a zwitterionic form of the fluoran dye that is stabilized by hydrogen bond formation.

What Is Black Powder Composed of S-205 and Bisphenol A? The prepared black solid was proved by both HPLC and ^{1}H-NMR measurements to be a complex (**CDC**) having a definite molar ratio of 1:4 (S-205:bisphenol A), regardless of the preparation conditions. In **CDC**, the dye molecule S-205 takes a zwitterionic structure where a cation is mainly located at C9 (spiro-carbon) and an anion is on a carboxyl group. This was deduced by IR and ^{13}C-NMR spectroscopy. It should be noted here that the same IR spectra can be obtained by heating and melting a mixture of the fluoran dye and bisphenol A, which takes place on actual thermal paper when an image is thermally formed. These findings lead us to deduce that this black solid is indeed **CDC**, which is the origin of color formation and is composed of fluorane dye and bisphenol A. Although there is no direct proof, it is quite natural to assume that the hydrogen bonding between the zwitterionic structure of S-205 (acceptor) and bisphenol A (donor) acts as a major source of complex stability (Scheme 2). This can agree well with the findings that **CDC** loses its color easily in solvents with a hydrogen-bonding (either donor or acceptor) character. The role of hydrogen bonding in color formation between a fluoran dye and phenols was also suggested by Tokita et al.,[9] where they measured the ^{13}C-NMR spectra of a fluoran dye dissolved in liquid phenols at elevated temperatures. By monitoring the UV-vis peak intensities of the absorption maxima around 450 and 590 nm by changing the experimental temperature of the measurements, they evaluated the enthalpy gain by the hydrogen-bonding formation under their experimental conditions, which was reported to be around −42 to −54 kJ/mol. These figures can rationalize our proposal of **CDC** formation and isolation under our experimental conditions.[10]



Scheme 2.

CDC is a fragile complex susceptible to a solvent with high polarity, heat and humidity, which is in extremely good agreement with the actual behavior of the images on thermal paper. This, along with matching IR spectra of the image portion on the thermal paper with that of **CDC**, supports well an idea that **CDC** is indeed responsible for color formation on thermal paper.

Conclusion

We successfully prepared and isolated a color-developing complex between a fluoran dye and a phenol dye developer. By measuring the IR and ^{13}C-NMR spectra in solution and in a solid form, we deduced that **CDC** is composed of one molecule of a zwitterionic form of the dye and four molecules of bisphenol A. Chemical analyses proved that **CDC** is a metastable complex, and vulnerable to a solvent, prolonged heating, and solvents with high polarity, which is in extremely good agreement with the behavior of images on thermal paper. Based on this **CDC** color-developing mechanism, which is a departure from the conventional acid-base mechanism, we have extended our work into the design of completely new dye developers, the result of which will soon be reported.

Experimental

S-205 and the color developer bisphenol A were commercially available. S-205 was obtained from Yamada Chemical. Color-developing experiments and the preparation of the **C**olor **D**eveloping **C**omplex (**CDC**) were carried out using these commercially available compounds. The purity of the compounds was checked by measuring the melting point (S-205; 164 – 166.5 °C, bisphenol A; 158 – 159 °C). First, 0.52 g (1 mmol) of S-205 was dissolved in hot toluene (nearly boiling), to which 0.23 g (1 mmol) to 1.37 g (6 mmol) of bisphenol A was added and further heated to obtain a clear solution. This solution was placed in an ice bath, which lead to black precipitation formation at the bottom. This was rapidly collected and filtered with suction. The black solid was then washed a couple of times with cold toluene, and immediately placed together with filter paper in vacuo overnight. **CDC** was most easily available when a starting molar ratio of 1:2 was chosen.

UV-vis spectra were measured on a JASCOUVIDEC 610C UV-vis spectrophotometer. Reflection UV-vis spectra were taken on an MCPD 100 spectrophotometer (Otsuka Electronics). IR spectra were recorded by a Perkin Elmer FT/IR Spectrum 2000 spectrometer. Solution ^{1}H-, and ^{13}C-NMR measurements were carried out by a JEOL JNM-EX270 spectrometer in CD$_3$CN at 25 °C with reference to the (CH$_3$)$_4$Si standard. The NMR signal assignments were performed completely by using C,H-COSY and the 2D-NOE NMR technique. Solid state ^{13}C-NMR spectra (CP/MAS) of **CDC** were also measured on a Chemagnetics CMX-400 Infinity Spectrometer (^{13}C resonance frequency; 100MHz) with TOSS (Total Suppression of Sidebands) and Dipolar Dephasing pulse techniques. The dipolar dephasing CP/MAS technique is very effective to distinguish those carbon atoms with no attached hydrogen from other hydrogen attached carbons. FAB MS (Fast Atom Bombardment Mass Spectrometry) experiments were carried out on a JEOL JMS-AX500 mass spectrometer in m-nitrobenzyl alcohol matrix.

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6 At present, it is not clear why **CDC** can be formed with a definite molar ratio (S-205 : bisphenol A = 1 : 4). Preliminary semi-empirical molecular orbital calculations on the open-form of S-205 suggest that there exist four electron rich atoms which can function as proton acceptors (two carboxylate oxygen atoms and 2 alkylamino nitrogen atoms) in a molecule. It may reasonable to think that each hydroxy proton from four bisphenol A molecules can interact with these electron rich atoms in S-205 and form a 1 : 4 complex stabilized by the hydrogen bond. Further investigation is needed to clarify the structure of **CDC**. We are now in the process to get further structural information on **CDC**, and to elucidate the mechanism how the **CDC** is formed with a definite molar ratio.

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10 The barrier between (L; colorless lactone form) and (Z; black colored zwitterion form) forms of the fluorane compounds can be estimated approximately from the Eyring equation to correlate the rate constant (k_1) for the equilibrium and the activation free energy ($\Delta G^{\neq}$).

$$k_1 = k\,(kT\,/\,h)\,\exp(-\Delta G^{\neq}) \qquad \text{(A)}$$

where, k is transmission coefficient, h is Plank constant, and T is absolute temperature.

If we assume the half-life period (t) to distinguish the (L) and (Z) forms separetely is 1 day (86400 seconds) at ambient temperature, the rate constant k_1 can be calculated approximately to be $0.8 \times 10^{-5}\ \mathrm{s}^{-1}$ by using the following equation.

$$t = (\ln 2)\,/\,k_1 \qquad \text{(B)}$$

And then, obtained k_1 value and other necessary values as assumed $k = 1, T = 293$ K were put into the Eq. A to give $\Delta G^{\neq}$ value as about 100 kJ/ mol.