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Sensitization in the Photoconductance of Poly-*N*-vinylcarbazole

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The sensitization in photoconductive poly-*N*-vinylcarbazole was studied systematically. The sensitizers were conveniently divided into two types, *optical* and *chemical*. The optical sensitization occurs with a smaller content of a dye, which extends the photoconductivity spectrum to its absorption band. Effective optical (or dye) sensitizers are found to be themselves photoconductive and *n*-type cationic and to have a slow photoresponse. The chemical sensitization occurs through the formation of a charge transfer complex with a considerable amount of a Lewis acid. The simultaneous addition of optical and chemical sensitizers induces amplified or additive effects; an amplified effect is observed when a strong acid is employed as a chemical sensitizer. A sensitized system with a strong acid shows a very slow photoresponse and may have fairly deep traps which act as a cause of the memory effect.

In a previous paper,[1] the authors reported that *poly-N-vinylcarbazole* (PVCZ) film has a small peak of its action spectrum for photoconduction and that the threshold of its optical absorption is in the near-ultraviolet region. Because of its transparency, it is expected that this film is applicable to a transparent, sensitive, electrophotographic layer which prints by a conventional technique. However, pure PVCZ has a low potentiality as a material for electrophotographic purposes since it has only a slight sensitivity in the visible spectrum.

According to a patent by Kalle & Co.,[2] it is possible to sensitize the photoconduction of PVCZ film by the addition of a small amount of certain dyes or by the addition of Lewis acid-type organic compounds. The cause or mechanism of the sensitization is not clear in the patent. The present authors conjecture that the dye sensitization or optical sensitization in this case is analogous to that of cadmium sulfide or glass, which have been investigated by Nelson,[3-6] and that the chemical sensitization occurs by means of the formation of charge transfer complexes between PVCZ and the sensitizers. The terms "optical sensitization" and "chemical sensitization" are empirically proposed by the authors for the sake of convenience in the classification of sensitizers after the model of silver halide photography.

From this point of view, we have investigated the electrophotographic behavior of PVCZ thin films sensitized with commercial dyes or electron acceptor compounds, and have examined the combined effects on sensitization when two different types of sensitizers are added to the PVCZ matrix. Recently, Hoegl[7] presented a paper in which the photosensitometries of doped PVCZ with miscellaneous acceptors were studied. In view of his results, our view of charge transfer in chemical sensitization seems to be pertinent.

In this paper, the authors will describe the results obtained from systems to which about forty dyes and fifty chemical sensitizers have been added, from the standpoint of improving the practical electrophotographic sensitivity.

Experimental

Materials.—PVCZ powder (Luvican M-170, Badische A. G.) was purified by the reprecipitation method described in the previous paper.[1] The dyestuffs and chemical sensitizers used were the GR-grade reagents listed in Tables I and III.

The Addition of Dyestuffs.—To a 10% solution of PVCZ dissolved in purified methylene chloride, a 1% dye solution in methanol was dropped; then the solution was stirred until it was homogeneously colored by the dye.

The solubilities of dyes in such organic solutions were so small that the micro crystals of dyes were deposited if added in excess. By preliminary tests, the optimum concentrations of dyes were found to lie between 0.02 and 0.06%, where the sensitization data of the same dye showed no remarkable difference. To compare dye sensitizers, all the concentrations were fixed at 0.05% by weight.

The Addition of Chemical Sensitizers.—Lewis acid-type sensitizers, such as acids, acid anhydrides, aldehydes, ketones, quinones, and polynitrated derivatives, were used. Their solubilities in PVCZ varied. For example, 2-methylanthraquinone was soluble to 25%, whereas monochloroacetic acid was soluble to 3% and the polymer solution showed a co-

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[1] Y. Hayashi, M. Kuroda, K. Imura and A. Inami, *Chem. High Polymer* (*Japan*), **21**, No. 234, 557 (1964).

[2] German Pat. 1068115.

[3] R. C. Nelson, *J. Opt. Soc. Am.*, **46**, 13 (1956).

[4] R. C. Nelson, ibid., **48**, 948 (1958).

[5] R. C. Nelson, ibid., **51**, 1182 (1961).

[6] R. C. Nelson, ibid., **50**, 1029 (1960).

[7] H. Hoegl, *J. Phys. Chem.*, **69**, 755 (1965).

agulation tendency at this concentration. As a whole, except for the quinone compounds, they have low solubilities.

As it was troublesome to find the optimum concentration of each sensitizer, the addition quantities of the less soluble compounds were fixed at 1%, and those of the quinone groups, at 10%. For only a few good sensitizers (see Table II) were the optimum concentrations examined.

When sensitization with a dye - Lewis acid system was investigated, the Lewis acid was added to the above dye-polymer solution. The final solution was stirred until it became transparent. The process of film formation from the final solution was carried out by a method similar to that described in the previous paper.1)

Electrophotographic Sensitivities.—To compare the sensitivities of the specimens, the electrophotographic charge-decay method was used. In another paper8) the present authors have explained the physical aspects of the method, the principle of which is almost analogous to that of the ordinary method for measuring photoconduction. The experimental set-up is presented schematically in Fig. 1. The sample was mounted on a grounded aluminum turntable rotating at 78 r. p. m. Above the periphery of the disc, a corona wire unit, an exposure unit, and a probe of a sector-type electrometer were fixed. A specimen which had been stored in the dark for at least 48 hr. was positively charged at 7 kV. by the corona to a saturation potential. Then the corona discharge and the turntable were simultaneously stopped, and the dark decay due to the dark resistance was measured under the probe. Several seconds later, an incandescent light was applied to the specimen and the light decay was measured. An example of the recorded data is shown in Fig. 2. As a representation of sensitivity, the authors adopted the half-decay exposure, $E_{1/2}$, obtained from the diagram, which corresponds to the half-decay time, $t_{1/2}$.

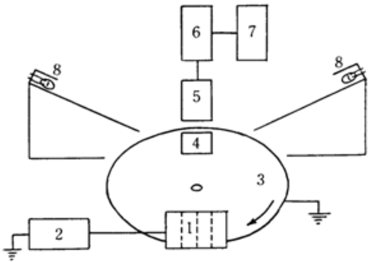

Fig. 1. Schematic representation of experimental set up for charge and light decay recording: 1, corona discharge device; 2, high voltage source; 3, turntable; 4, a sample; 5, 6, electrometer probe and amplifier; 7, recorder; 8, light sources.

In order to study the spectral sensitivity, a charged specimen was put into a grating spectrograph (Narumi & Co., investigated by J. Koana).9) The surface exposed to the continuous spectrum generated a latent static image. A negatively-charged xerographic toner was then dispersed onto the surface, and the visible image was printed. All the processes mentioned above were carried out in the dark.

Photoconductivity.—The photoconductivity was measured by using the same types of cells and apparatus as have been described in a previous paper.1)

Optical Absorption.—A photometer (Hitachi EPS-II) was used for the determination of the optical absorption. The samples used were of a dilute solution in a certain medium or of a solid, thin film laminated onto a quartz plate by the same method as used with the conductivity cell.

Results and Discussion

Spectral Responses of Sensitized Systems by a Conventional Electrophotographic Technique.—We classified the sensitizers into two types, the optical sensitizers and the chemical sensitizers.

From the spectral responses obtained by a grating spectrograph, we found that the dye sensitization was similar to the optical sensitization with dyes used in silver-halide photographic techniques. For instance, a spectral response of the PVCZ-crystal violet system is shown in Fig. 3B. In addition to the original small response at 356 mμ, a large peak is found at 592 mμ which corresponds to the optical absorption or photoconduction peak of crystal violet.

As an example of chemical sensitization, a spectral response of the PVCZ - trichloroacetic acid system is presented in Fig. 3C, where the exposure time was 5 min. The behavior in a longer exposure is shown in Fig. 3D. Here, in addition to the amplified original response of PVCZ, the series of peaks between 400 mμ and 600 mμ is found. This fact seems to be contrary to our assumed definition of chemical sensitization. However, when the single system of PVCZ has been exposed for 2 hr., a similar series of peaks was found (see Fig. 3E).

This series of peaks appears to be due to sensitization by unknown original impurities; this impurity sensitization effect seems to be so small that no response can be found by the ordinary method of photoconductivity measurement described in our previous paper.

With other chemical sensitizers, the peaks are amplified as well as with trichloroacetic acid, and the impurity effect is also observed. Upon the addition of only a chemical sensitizer, the PVCZ film becomes a little more sensitive in tungsten light, and its sensitization is of the order of a bad dye sensitizer.

As is shown in Fig. 3F, picric acid behaves as another type of chemical sensitizer. As a whole, acid, acid anhydrides, aldehydes, and ketones which were colorless behave as chemical sensitizers.

Next, an example of the photoresponse of a

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8) A. Inami, K. Morimoto and Y. Hayashi, This Bulletin, **37**, 842 (1964).

9) Z. Koana and Z. Wakimoto, *Electrophotography* (*Japan*), **2**, No. 1, 8 (1960).

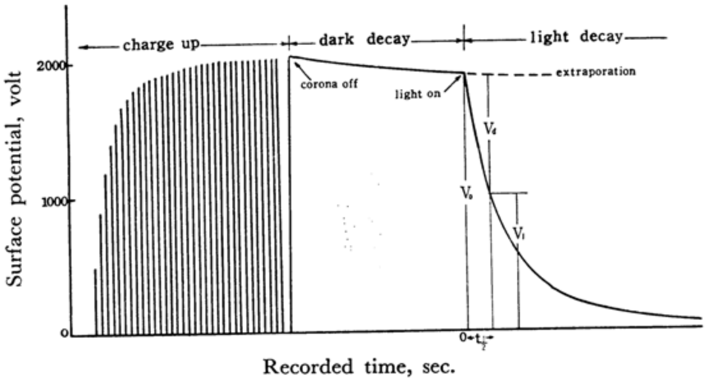
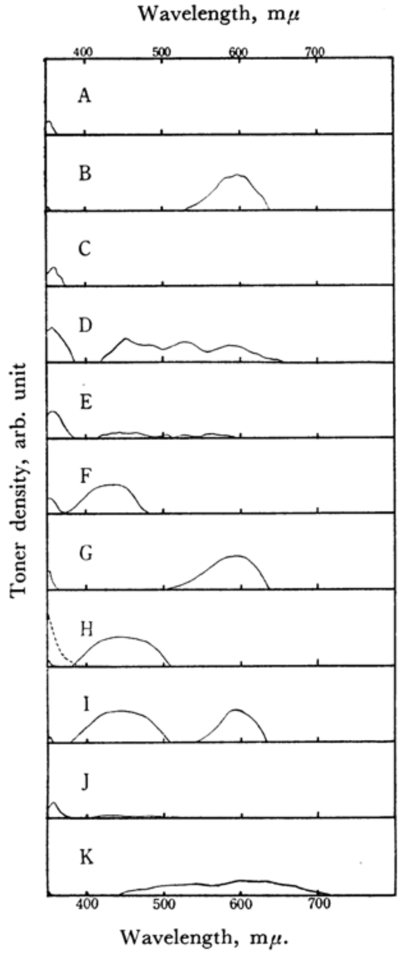


Fig. 2. A recorded example of charge build up and decay curve obtained by the apparatus in Fig. 1. V_0 means an initial potential. The time when V_l/V_d reduces to a half is arranged as $t_{1/2}$.



	Exposure period sec.	Sensitizer
A	1200	None
B	60	Crystal violet: 0.05%
C	300	Trichloroacetic acid: 1%
D	1200	Trichloroacetic acid: 1%
E	7200	None
F	1200	Picric acid: 1%
G	5	Crystal violet: 0.05% Trichloroacetic acid: 1%
H	30	2-Methylanthraquinone: 10%
I	30	2-Methylanthraquinone: 10% Crystal violet: 0.05%
J	1200	Pinacyanole: 0.05%
K	60	*p*-Chloranil, 10%

Fig. 3. Spectral responses of some sensitized or unsensitized samples by grating spectrographic measurements.

system formed of three components (PVCZ-crystal violet-trichloroacetic acid) is presented in Fig. 3G. Upon the addition of trichloroacetic acid, the spectral response of crystal violet at 600 mμ becomes very high after only five seconds' exposure (cf. Fig. 3B).

On the other hand, sensitized systems with a quinone compound behave differently than with the five kinds of Lewis acids mentioned above. As may be seen in Fig. 3H, the spectral response of the PVCZ-2-methylanthraquinone system has a peak in 440 mμ, while its optical absorption spectrum rises at 400 mμ and shows a strong and broad absorption to the short wavelength side (dotted line in Fig. 3H). The peak wavelength at 440 mμ obtained by the electrophotographic process has been found by our preliminary experiment[*1] to correspond with the wavelength of the photoconduction peak of 2-methylanthraquinone itself.

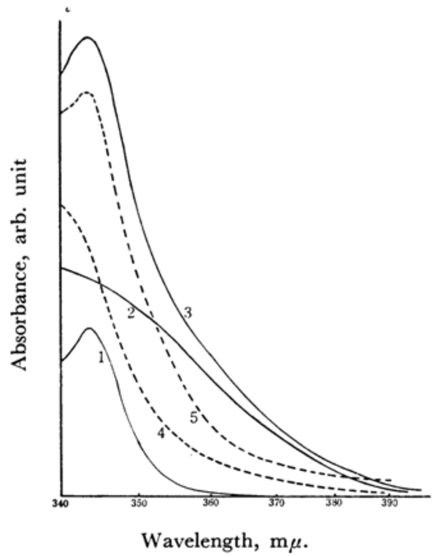


Fig. 4. Absorption spectra of picric acid and 2-methylanthraquinone (dotted line) doped samples: 1, pure PVCZ; 2, pure picric acid; 3, equivalent mixture of 1 and 2; 4 pure 2-methylanthraquinone; 5, equivalent mixture of 1 and 4. All samples are diluted with *sym*-dichloroethane.

Almost all the quinone compounds investigated here show the same sensitization as 2-methylanthraquinone. From these results the members of the quinone group which are classified as "chemical sensitizers" might rather be called "optical sensitizers." The quinones are as photoconductive themselves as such optical dye sensitizers as triphenylmethane or cyanine dyes. However, we dare to regard them as chemical sensitizers because the difference in effective amount is found to be appreciable between quinones and dyes.

Absorption Spectra in Sensitized Systems.—It is assumed that a new peak absorption spectrum which belongs to neither PVCZ nor a sensitizers may be realized if a chemical reaction or a charge transfer occurs between them. A part of the dye sensitizers are considered to be adsorbed in the amorphous regions of the polymer in the dried glassy state. However, no new absorption spectrum was found in the PVCZ-dye system.

No chemical sensitizers (except *p*-chloranil) which are regarded as usual electron acceptors afford any new absorption band when mixed with PVCZ. When a chemical sensitizer is added, the intensity of the absorption of PVCZ increases considerably in comparison with that of the parent polymer. Upon the addition of some quinones or polynitrated derivatives, such as 2-methylanthraquinone or picric acid, a slight red shift of the long wavelength edge of the spectrum

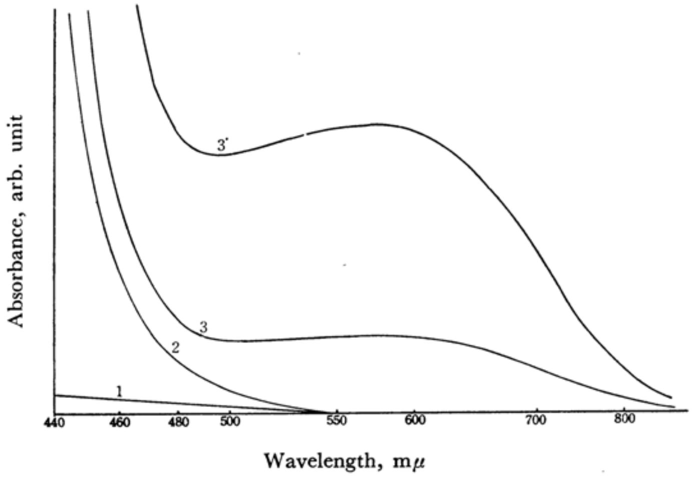


Fig. 5. Charge transfer band of *p*-chloranil doped sample: 1, pure PVCZ; 2; pure *p*-chloranil; 3, equivalent mixture of 1 and 2; 3′, twice of 3 in conc. All samples are diluted with benzene.

[*1] From a spectral response measurement on 2-methylanthraquinone film evaporated on NESA glass (for a sandwich cell), we found a weak response peak at 440 mμ.

occurs. Figure 4 presents curves showing the red shifts produced by the addition of picric acid or 2-methylanthraquinone.

Chloroanil, which is well known as a strong acceptor, produces a new peak at 574 mμ as a result of forming a charge transfer complex with the polymer (Fig. 5). The shape of the broad charge transfer band (between 500 and 800 mμ) coincides with the electrophotographic spectral image in Fig. 3K, indicating that the chloranil sensitization is due to the formation of a new absorption band in the visible spectral region.

Optical (Dye) Sensitizations.—From Table I, crystal violet, methyl violet, and malachite green (triphenylmethane derivatives) rhodamine 6G, rhodamine B (xanthene derivatives), and methylene blue (thiazine derivative) may be seen to be good sensitizers. All of them have $=\mathrm{N}^+<$ and are called basic dyes (or cationics).

Acid violet 6B and naphthalene green from triphenylmethane, and acid rhodamine G, eosine A, eosine S, fluorescein, rose bengale, and phloxine from xanthene are all acidic dyes (or anionics). From Table I, an interesting tendency is found: the effective dyes for PVCZ sensitization are not acidic dyes but cationics. As in rhodamine homologues, a sulfonated derivative, namely, sulforhodamine B (acidic), shows a considerably weak sensitizability compared to rhodamine B (basic). The oil-soluble nonionic dyes show no effect.

Nelson suggested that there is a general tendency for cationic dyes to be *n*-type and anionic *p*-type conductors.(10) In Table II, some dyes which have already been classified experimentally into the *p*- or *n*-type by other authors are summarized. From this table it may be seen that most *n*-type dyes seem to be effective for PVCZ except pinacyanole. This result contrasts with a considerable effect of acidic *p*-type dyes in the zinc oxide (*n*-type) photosensitive layer of the Electrofax*2 process. In the previous paper, the present authors specified that the sign of charge carriers in PVCZ might be positive. Judging from this fact, there seems to be an empirical tendency for an organic *p*-type photoconductor to become more sensitive when doped with an *n*-type dye.

Pinacyanole, which is a good sensitizer for cadmium sulfide crystal, shows no effect. In Fig. 3J, no peak is found at the wavelength of 640 mμ, which is an absorption peak of the dye in the visible region. According to the works of Terenin(11) and Nelson,(3) a dye sensitization may occur by the following processes: electron-hole pairs (they might better be called "excitons") are produced by light; then they are separated

TABLE I. SENSITIZATIONS WITH DYES

Dye	Sensitivity, $E_{1/2}$, lux.sec.
Triphenyl Methanes	
Victoria pure blue	1137
Victoria blue	612
Crystal violet	350
Brilliant green	420
Methyl violet	1015
Acid violet 6B	10850
Fuchsine	none
Basic cyanine BX	612
Basic cyanine 6G	4550
Malachite green	490
Auramine	13300
Naphthalene green	none
Xanthenes	
Rhodamine 6G	657
Acid rhodamine G	none
Rhodamine B extra	725
Fluorescein	none
Rose bengale	none
Sulforhodamine B	4290
Eosine A	6300
Eosine S	5250
Phloxine	15750
Azines	
Phenosaflanine	6650
Pinacryptol green	13300
Selestine blue	none
Acridines	
Pinacryptol yellow	2800
Acridine orange	3355
Tripafravine	5900
Triazines	
Methylene blue	1750
New methylene blue	402
Cyanines	
Chinoline blue	42000
Pinacyanole	none
1, 1′-Diethyl-4, 4′-quinocarbocyanine iodide	40000
1, 1′-Diethyl-4, 4′-quinocyanine iodide	22000
3, 3′-Diethyl-thiacarbocyanine iodide	8250
3, 3′-Diethyl-2, 2′-thiacyanine iodide	15500
2-(*p*-Dimethylaminostyryl)-benzothiazole-ethiodide	4650
1, 1′-Diethyl-2, 4′-quino cyanine iodide	16000
Azo dyes	
Oil red B	14000
Chrom blue black RC	none
Butter yellow	14000
Fast light yellow G	none
Neutral red	8205
Anthraquinones	
Quinizarin	1260
Alizarin	9800

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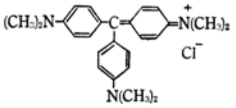
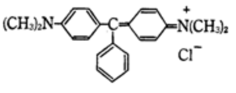
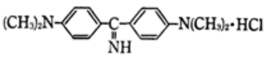
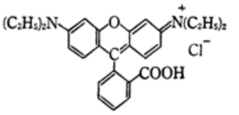
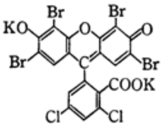
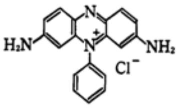
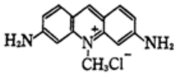
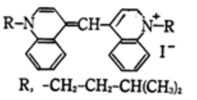
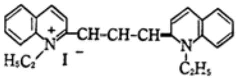
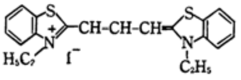
10) R. C. Nelson, *J. Mol. Spectroscopy,* **7**, 439 (1961).

*2 A trade mark of the Radio Corporation of America.

TABLE II. COMPARISON OF SENSITIZABILITIES OF SOME DYES WHICH HAVE BEEN DECIDED ON *p*- OR *n*- BY OTHER AUTHOURS

Dye	Chemical formula	$E_{1/2}$ lux. sec.	Type of *p*- or *n*-	Reference
Crystal violet		350	*n*	Terenin et al.[12]
Malachite green		490	*n*	Terenin et al.[12]
Auramine		13300	*p*	Terenin et al.[12]
Rhodamine B extra		725	*n*	Terenin et al.[12] Takahashi et al.[13] Hauffe et al.[14]
Phloxine		15750	*p*	Takahashi et al.[13]
Phenosafranine		6650	*p*	Terenin et al.[12]
Tripaflavine		5900	*p*	Terenin et al.[12] Terenin et al.[13]
Chinoline blue		42000	*p*	Terenin et al.[12]
Pinacyanole		none	*n*	Terenin et al.[12]
3, 3′-Diethylthiacarbocyanine iodide		8250	*p*	Terenin et al.[12]

into charge carriers, which are injected into *N*-vinylcarbazole unit molecules.*[3] If all dye sensitization were caused by this process, pinacyanole in cyanines should be just as effective as crystal violet in triphenylmethanes.

It may, therefore, be assumed that the difference in sensitization ability between pinacyanole and crystal violet may be casued by a difference in their photoconductive characteristics in their pure, solid states. There are many triphenylmethane dyes with slow responses of rise and decay, while pinacyanole has a very rapid response.[11] Moreover, the former has many trapping centers, while the latter is considered to have fewer.[10] From these facts, the electron-hole pairs produced by irradiation may not separate easily and are likely to have a longer life in the case of crystal violet than in that of pinacyanole.*[4] As the distance between dye molecules in the polymer is considered to be rather longer than

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*[3] We substitute the inorganic photoconductive substrates (e. g., cadmium sulfide, zinc oxide, silver halide, etc.) for a vitreus polymeric photoconductor.

11) A. Terenin, "Electrical Conductivity in Organic Solids," Interscience Publ., New York (1961), p. 39.

*[4] Although this assumption should be employed in the pure solid, we dare to make a deduction by applying it to a diluted state of a dye in the polymer.

12) A. Terenin, *Proc. Chem. Soc.*, 321, Sep. (1961).

13) T. Takahashi, C. Shishido, H. Hori and M. Wada, *Electrophotography* (*Japan*), **3**, No. 3, 9 (1961).

14) K. Hauffe and J. Kaufhold, *Z. Electrochem.*, **66**, 316 (1962).

TABLE III. SENSITIZATIONS WITH A DYE AND/OR LEWIS ACIDS

	Without dye $E_{1/2}$, lux.sec.	With crystal violet $E_{1/2}$, lux.sec.
Acids and acid anhydrides		
Acetic acid	none	217
Monochloroacetic acid	10500	49
Dichloroacetic acid	5880	46
Trichloroacetic acid	3745	26
Monobromoacetic acid	11900	75
Tribromoacetic acid	13850	553
Benzoic acid	none	196
Tetrachlorophthalic acid	1595	112
Tetrachlorophthalic anhydride	3910	110
Succinic anhydride	39200	142
Maleic acid	7175	84
Maleic anhydride	11270	166
Telephthalic acid	none	350
Cinnamic acid	5250	143
Phthalic acid	4100	73
Phthalic anhydride	4230	85
Acetanilide	none	80
Benzenesulfonic acid	none	78
p-Toluenesulfonic acid	none	85
Phenol	none	2170
p-Nitrophenol	5950	85
Picric acid	650	36
Ketones		
Acetophenone	none	287
Benzoine	11600	245
Benzil	6800	270
Aldehydes		
p-Nitrobenzaldehyde	1030	287
o-Nitrobenzaldehyde	1350	325
2, 4-Dichlorobenzaldehyde	none	441
p-Dimethylaminobenzaldehyde	none	280
p-Hydroxybenzaldehyde	none	860
Furfural	none	175
Bromal	900	77
Quinones		
p-Quinone	2850	1103
p-Chloranil	1100	560
α-Naphthoquinone	1295	297
Anthraquinone	577	175
1-Aminoanthraquinone	1190	332
2-Aminoanthraquinone	490	280
1, 4-Diaminoanthraquinone	9325	9975
1-Nitroanthraquinone	297	140
1, 5-Dichloroanthraquinone	402	241
2-Chloroanthraquinone	595	260
2-Methylanthraquinone	621	186
2, 6-Dichloro-*p*-benzoquinone	665	224
1, 2-Benzanthraquinone	297	200
Anthraquinone-2-carboxylic acid	630	149
Anthraquinone-2-sulfonic acid	none	190
Polynitrate		
Trinitrobenzene	435	252

that in the pure, solid state, the longer the life of the electron-hole pair, the higher the injection probability for the polymer will be.

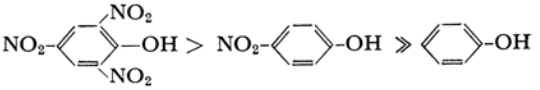
From Table I, crystal violet may be found to be the best optical sensitizer. Therefore, we adopted it as the dye component for tertiary systems (PVCZ, dye and Lewis acid). In the next section, the sensitivities of binary systems (PVCZ and Lewis acids) and of tertiary systems will be compared (see Table III).

Chemical (Lewis Acid) Sensitization.—Under the practical incandescent light used for electrophotography, usual acid and ketone derivatives are almost ineffective. On the other hand, picric acid in the acid group, *p*-nitroaldehyde, bromal in aldehydes, and most quinones are effective. It can be said that all of these effective chemical sensitizers are slightly colored themselves, and even after being doped into PVCZ solutions, they maintain their original color fairly well. (As a special case, chloranil changed from its original color (pale yellow) to dark green.)

From Table III, we can deduce the following information: with a small amount of crystal violet, an acid shows a tendency to sensitize more in conformity with an increase in the halogenation or nitration degree in its homologue; i. e.,

$$Cl_3CCOOH,\ Cl_2CHCOOH > ClCH_2COOH \gg CH_3COOH$$

or



It is known that trichloroacetic acid is a stronger acid than di, mono, or unsubstituted acetic acid because of the inductive effect by Cl, the key atom. The same behavior exists in the latter case of the phenol homologue. Next, free acids are stronger sensitizers than anhydrides; i. e.,

maleic acid > maleic anhydride
phthalic acid > phthalic anhydride

These results suggest that the acidity seems to be a key point in the sensitization ability in white incandescent light when an effective dye is used. Colorless aldehydes also behave in the same way as colorless acids.

As has been mentioned above, these colorless acids, aldehydes, or ketones have a small effect in the visual spectral region when the smaples have been exposed for long periods. However, in the practical exposure of the electrophotographic process, these samples show no response.

Each quinone investigated here has a fair sensitization ability without a dye except for anthraquinone-2-sulfonic acid, which is less soluble to the polymer than the other quinones. As a dye is added, anthaquinone-2-sulfonic acid becomes sensitive. Thus, the acidic group ($-SO_3H$)

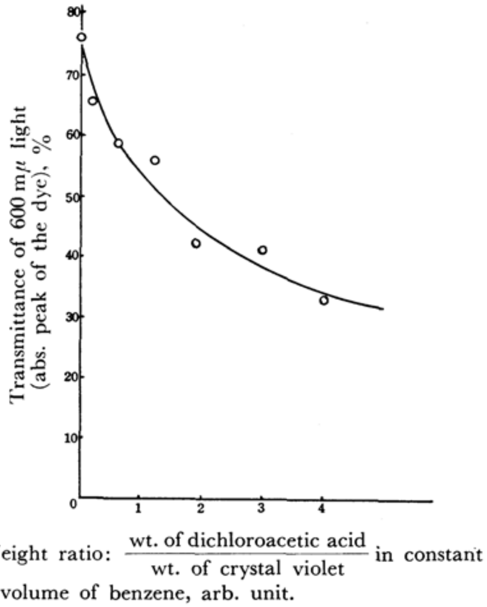


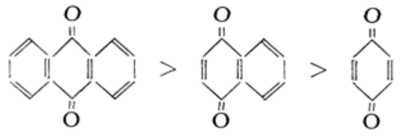
Fig. 6. Variation of solubility of crystal violet to benzene with increase of dichloroacetic acid concn.

seems to play a subsidiary role in the dye sensitization.

Some quinones were found to be organic photoconductors similar to many dyestuffs. Some anthraquinone and naphthoquinone derivatives are themselves dyestuffs or the intermediate products of dyestuffs.

These facts suggest that the members of the quinone group may be classified as optical sensitizers. However, their effective quantities are considerably larger (1—10%) than those of the dyes (10^{-3}—10^{-2}%); that is, as has been stated in the foregoing section, 2-methylanthraquinone is soluble into PVCZ to 20% by weight. The difference in effective concentration between quinones and dyes suggests some discrepancies between their sensitizing mechanisms.

Regarding the quinone group, the following empirical tendency is obtained from Table III:



Thus the numbers of aromatic π electrons may contribute to the sensitization ability.

Polynitrated aromatic compounds, such as trinitrobenzene and picric acid, are good sensitizers under an incandescent light. Each of them has a slight yellowish color initially; the original slight yellow deepens bathochromatically when joined in a PVCZ solution. With 2-methylanthraquinone this tendency is also observed. This phenomenon is related clearly to a slight red shift in Fig. 4 (dotted line); it can be explained in terms of the formation of a weak charge transfer complex between 2-methylanthraquinone or picric acid and PVCZ. Picric acid seems to have two sensitizing functions, as acid and as nitro compound.

A chloroanil-added sample had a low sensitivity in spite of forming a stable charge transfer complex. Its optimum exposure in the electrophotographic process was 1500 lux. sec., about twice

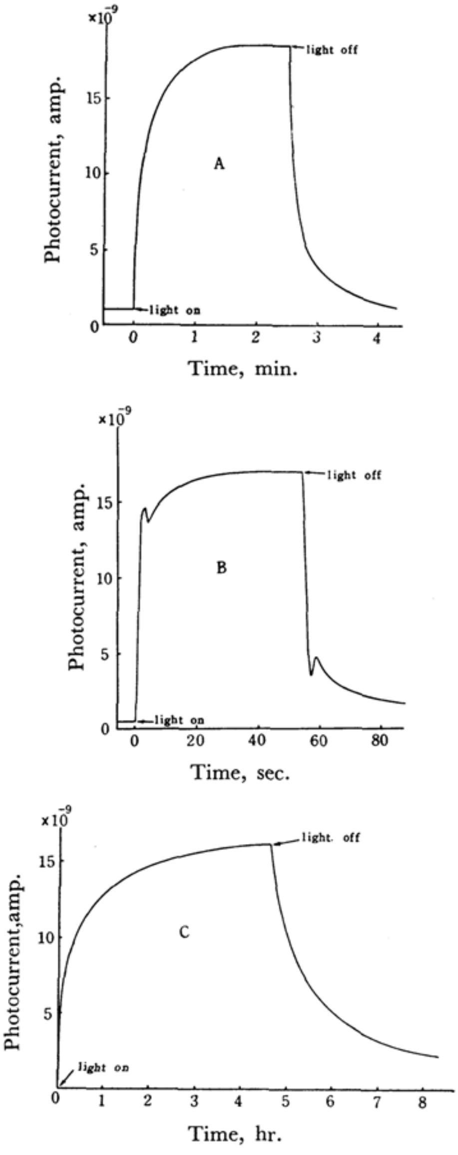


Fig. 7. Photoconduction responses on sandwich cells of PVCZ and the sensitized systems: A, PVCZ, 2μ (thickness), 5V. (applied voltage), 1000 lux. (illuminance); B, PVCZ with crystal violet 0.05%, 2μ, 5V., 20 lux.; C, PVCZ with 0.05% of crystal violet and 1% of trichloroacetic acid, 57μ, 10V., 100 lux., the illuminated electrodes positive, 3.1 cm^2 in area.

that in the foregoing two. One reason for this result may be the considerable decrease in dark resistivity with the formation of a charge transfer complex.

The Combined Effect of a Dye-acid System.—As has been mentioned in the foregoing section, an acid is an effective chemical sensitizer when used with a dye. It was observed that all the cationic dyes investigated dissolve slightly in benzene, and that their solubilities increase upon the slight addition of an acid. Figure 6 shows an example of the use of crystal violet and dichloroacetic acid. It is there shown that the solubility of crystal violet in benzene increases with an increase in the amount of dichloroacetic acid added. Consequently, the dye dispersion is converted into a solution and the chain unit of the polymer seems to be dyed smoothly.

Figure 3G indicates that an amplified sensitization is achieved by the PVCZ-dye-acid system in comparison with a system containing only a dye (Fig. 3B). On the contrary, the PVCZ - crystal violet - 2-methylanthraquinone system shows only an additional sensitization (Figs. 3H and I). An ordinary photoconduction measurement clearly shows that the response rate of the PVCZ-trichloroacetic acid system is much lower than that of the PVCZ - 2-methylanthraquinone system or the PVCZ - crystal violet system (Figs. 7A, B, and C). A chemical sensitizer with an amplification ability with a dye seems to show a slow rise and then a decay in its photoconduction response. Such a chemical sensitizer may increase the number of carrier-trapping centers as well as the number of photo-induced carriers.

Fatigue in the Photoresponse upon Repeated Use.—It is well known that a vitreus selenium layer loses its electrophotographic sensitivity upon the repetition of the charge-light decay cycle within a short period because of the space charge generation by trapped holes. To examine such memory effects in the organic photoconductors, a few higher sensitive systems were investigated. An example of the effect of repetition on a PVCZ-crystal violet - trichloacetic acid system is shown in Fig. 8. In one cycle, the sample was charged up by a positive corona discharge of 7000 V. for 1 min.; after it had then been put in the dark for 10 sec., it was exposed with an incandescent light of 500 lux. for 30 sec. The initial voltage, V_0, decreases and $E_{1/2}$ increased with the repetition of the cycle. Only at the tenth cycle was the exposure period extended to 10 min.; the conditions after the eleventh cycle was similar to the starting conditions. The dark voltage and $E_{1/2}$ at the eleventh cycle were very low and high respectively;

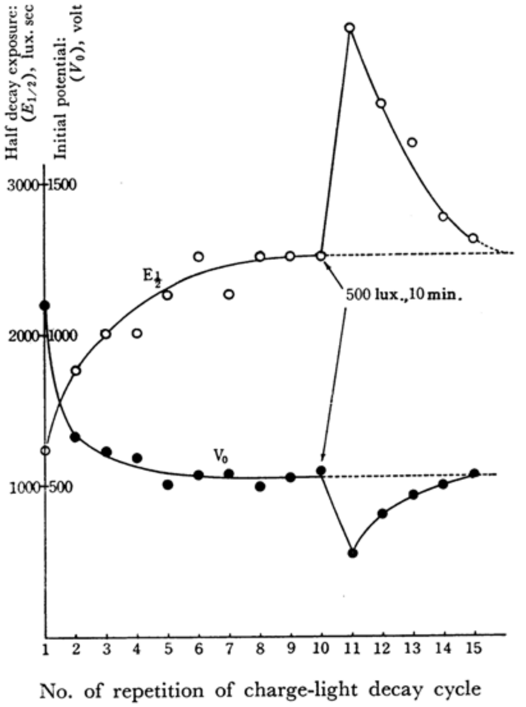


Fig. 8. Variation of V_0 or $E_{1/2}$ with incease of number of repetition, ●, V_0; ○, $E_{1/2}$. The sample is same as 6 in Fig 9.

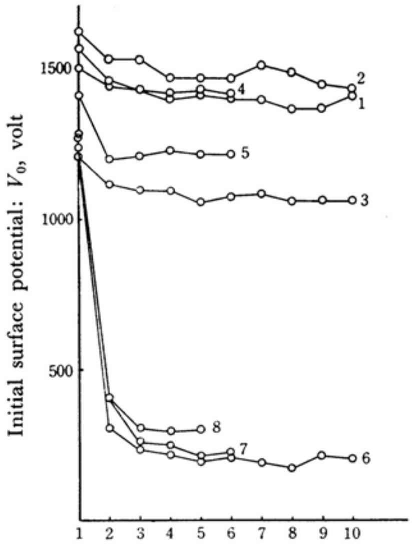
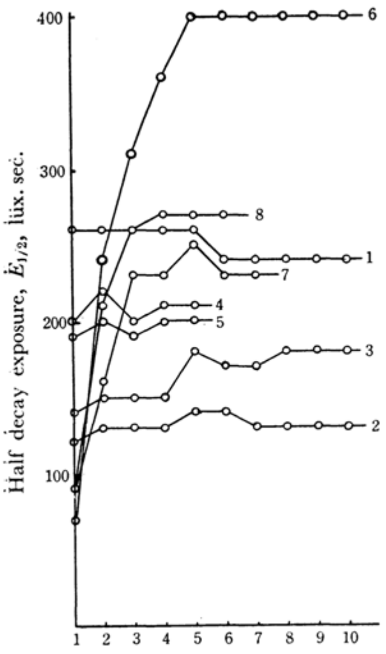


Fig. 9. Variations of V_0 with increase of repetition cycles.
1, PVCZ with 0.05% of crystal violet; 2, PVCZ with 0.05% of crystal violet and 10% of 2-methylanthraquinone; 3, PVCZ with 10% of chloranil; 4, PVCZ with 0.05% of crystal violet and 1% of acetophenone; 5, PVCZ with 0.05% of crystal violet and 1% of *p*-dimethylamino benzaldehyde; 6, PVCZ with 0.05% of crystal violet and 1% of trichloroacetic acid; 7, PVCZ with 0.05% of crystal violet and 1% of picric acid; 8, PVCZ with 0.05% of crystal violet and 1% of bromal.



No. of repetetion of charge-light decay cycle

Fig. 10. Variations of $E_{1/2}$ with increase of repetition cycles on the same samples listed in Fig. 9.

when they approached the dotted saturation lines with repetition cycles. After the eleventh exposure, the values should have lain on the extraporated constant line if a longer exposure had not been applied at the tenth cycle. The constant line may result from the balance between the fatigue by irradiation and the recovery by the high tension given in the dark. The fatigue is to be attributed to irradiation and not to charging.

In Figs. 9 and 10, the variations in V_0 and $E_{1/2}$ are shown. The dye-added sample (1) and the quinone-added sample (2) show few memory effects. Weak acid-added samples (4, 5) show the same. On the other hand, the samples with strong acids or strong acceptors (6, 7, 8) have large variations. These characteristics are parallel to the results from the photoconduction measurements described in the foregoing section. As is shown in Fig. 7B, a sample sensitized with crystal violet alone quickly loses its resistivity to a certain value upon irradiation, and then it turns back to the original value after the light is switched off. In the case of strong acids or strong acceptors, these responses are very slow. From these results, the fatigue (in other words, the hysteresis) is assumed to occur through the traps of carriers.

Some Aspects in Charge Porality.—Hoegl reported that a system of PVCZ doped with a Lewis acid-type acceptor (e. g., chloranil, anthraquinone and TCNE) acts as a *p*-type photoconductor because it has a higher discharge rate when positively charged than when negatively charged. In this case the dopants are assumed to be traps for electrons. Our data from the photoconduction measurements show similar results. In Fig. 11, a large photocurrent value is observed for the PVCZ-crystal violet - trichloroacetic acid system when the illuminated electrode is positive. On the other hand, the data from the charge decay method showed little difference between the two sign-charged samples. Actually in a practical process in electrophotography, the optimum printing exposure of a positively-charged sample is equivalent to that of negatively-charged one.

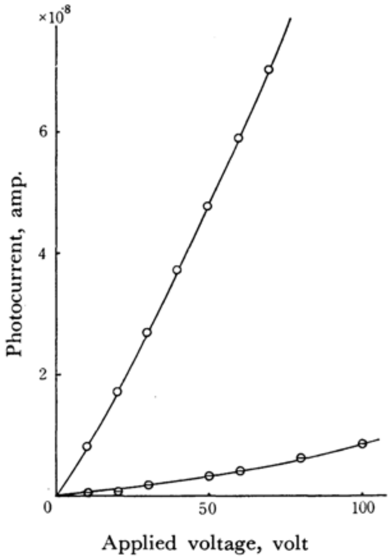


Fig. 11. V-I relations of sandwich cell as the illuminated electrode is positive (○) or negative (⊖) respectively: 20 lux. (illuminance), the same sample as used in Fig 7C.

Conclusions

From the studies of sensitization in photoconductive poly-*N*-vinylcarbazole, some conclusions can be deduced: (1) It is convenient to divide the sensitization into two types, "optical sensitization" and "chemical sensitization." The former occurs at a smaller dye content, which extends the photoconduction spectrum of the polymer to the dye's absorption bands, while the latter is induced by the formation of a charge transfer complex in the presence of a considerable amount of a Lewis acid; (2) The most effective dyes are *n*-type cationics with slow photoresponses in their pure, solid states; (3) In the sensitization with two different types of components (dye and Lewis acid), an amplified effect or an additive effect is obtained. The former case occurs frequently when a strong acid is employed as a chemical sensitizer; (4) A sensitized system with a strong acid shows very slow rates of rise and decay in the photoconduction measurements.

Although the systems containing strong acids show high sensitivities ($E_{1/2}<100$), they are not always of practical use for electrophotography because of their rapid dark decays and their intense memory effects.

The most useful photoconductive systems are those containing quinones, in spite of their showing only additive effects with crystal violet. 2-Methylanthraquinone is especially useful: (1) its solubility with PVCZ is large, (2) its charge transfer color is pale, and (3) its memory effect is very small. The xerographic characteristics of the practical sample were as follows. The maximum and minimum image densities were 3.0 and 0.1 respectively; the exposure was about 300 lux. sec. at the optimum range, and the γ value was 1.5 when a commercial xerographic toner was used.

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