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Sensitization in the Photoconductance of Polyacenaphthylene

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The sensitization of the photoconductivity in polyacenaphthylene by a dye and/or a Lewis acid was investigated. The most effective materials are methylene blue ($E_{1/2}$=1500 lux. sec.), rhodamine 6G (6000 lux. sec.), and victoria pure blue (6500 lux. sec.) in the dye sensitization, and 1-nitroanthraquinone (1200 lux. sec.), 2, 3-dichloronaphthoquinone (1400 lux. sec.), 1, 5-dichloroanthraquinone (1500 lux. sec.), chloranil (1800 lux. sec.), and 2-chloroanthraquinone (1900 lux. sec.) in the Lewis-acid sensitization. The combined effects of a dye and a strong acid were determined in the case of polyacenaphthylene as well as poly-*N*-vinylcarbazole.

In a previous paper,1) the authors reported that polyacenaphthylene showed only a low photoconductivity, while the nitrated polymer obtained by the partial nitration of polyacenaphthylene showed a considerable photoconductivity. The effect of the nitration on photoconductivity may be interpreted by means of a charged transfer mechanism. The nitrated acenaphthylene group is considered to be an electron acceptor. This process may be called the intramolecular chemical sensitization. Slough studied the semiconductivity of charge transfer complexes of polyacenaphthylene with Lewis acids in the dark,2) and Hoegl reported in a recent paper that a charge transfer complex of polyacenaphthylene doped with hexabromonaphthalic anhydride could be made to show photoconductive behavior with the aid of the electrophotographic printing process.3) The present authors found the same behavior: polyacenaphthylene, which is regarded as a polymeric donor, is sensitized by doping miscellaneous dyes and/or Lewis acids, just as poly-*N*-vinylcarbazole can be sensitized with them.4)

This paper will report the experimental results obtained by adding dyes and Lewis acids to polyacenaphthylene in order to determine a useful composition of photosensitive material for the electrophotographic process.

Experimental

The Polymerization of Acenaphthylene.5)—Ten grams of acenaphthylene was dissolved in 10 ml. of ethyl benzene and emulsified with 100 ml. of a sodium stearate solution.*1 As an initiator, 0.4 g. of potassium persulfate was added to the emulsion; then the mixture was agitated in a closed container for 10 hr. at 45°C. The resultant polymer was coagulated from the solution by dropping it slowly into dilute hydrochloric acid. The coagulated polymer was then filtered off, dissolved in benzene, and precipitated into methyl alcohol. Yield, 74%; [η]=0.53 (at 25°C in benzene).

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1) A. Inami, K. Morimoto and Y. Hayashi, This Bulletin, **37**, 842 (1964).
2) W. Slough, *Trans. Faraday Soc.*, **58**, 2360 (1962).
3) H. Hoegl, *J. Phys. Chem.*, **69**, 755 (1965).
4) Y. Hayashi, M. Kuroda and A. Inami, This Bulletin, **39**, 1660 (1966).
5) U. S. Pat. 2563524 (1951).

[*1] This emulsion consisted of 600 ml. of water, 14 g. of stearic acid, and 6 g. of potassium hydroxide.

The Preparation of a Photosensitive Specimen.—The method of preparation was substantially the same as to that used for poly-*N*-vinylcarbazole and reported previously.[4] Here, toluene was used as the solvent, and the dye concentration was fixed at 0.05% by weight for the solid polymer powder. The Lewis acids (chemical sensitizer) concentrations were fixed at 1% by weight in the case of acids, acid anhydrides, aldehydes, and ketones. In the case of the quinone group, however, all the addition amounts were fixed at 10%.

The final polymer solutions were coated onto aluminum plates 0.1 mm. thick with the aid of a Baker-type applicator; then the solvent was thoroughly evaporated in the drying oven. After the solvent had been evaporated, the specimen films were about 15 μ thick. The parent polymer was so brittle in the thin film form that, after the solvent had been evaporated, numerous cracks generated if the drying speed was too high. Therefore, the drying temperature was kept below 50°C at atmospheric pressure.

Sensitometry.—The photoconductive sensitivities of the doped samples were measured by the electrophotographic charge-decay method described in previous papers.[1,4] The sensitivities were represented as the half decay exposure, $E_{1/2}$, which serves as an index of the photoconduction. In this experiment, two light intensities were applied, i. e., 1000 lux. in less sensitive materials ($E_{1/2}>1000$ lux. sec.), and 100 lux. in highly sensitive materials ($E_{1/2}<1000$ lux. sec.). In order to indicate the dark decay due to the dark resistivity of a sample, the initial voltage, V_0, at the starting point of the light decay is listed along with $E_{1/2}$. These data were obtained at a constant temperature (20°C) and humidity (50%).

Results

Dye Sensitization.—It can be seen from Table I that the most effective dye is methylene blue ($E_{1/2}=1500$ lux. sec.), and the next is rhodamine 6G ($E_{1/2}=6000$ lux. sec.). Crystal violet, rhodamine B, and malachite green, which were very effective on poly-*N*-vinylcarbazole, show a lower sensitizability than the foregoing.

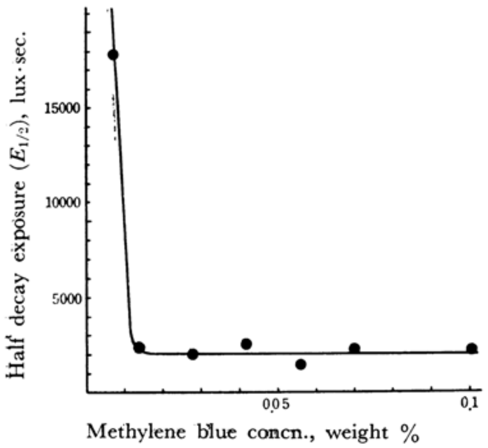

Fig. 1. Relation between sensitivity of dyed polyacenaphthylene and methylene blue concn.

Table I. Sensitizations by dyes

	V_0, V.	$E_{1/2}$ lux.sec.
Phenylmethanes		
Victoria pure blue	1660	6500
Victoria blue	1540	>100000
Crystal violet	1520	>100000
Brilliant green	1050	20000
Acid violet 6G	1720	73000
Fuchsin	2280	27000
Basic cyanine BX	1760	11000
Malachite green	1720	9000
Auramine	1520	75000
Naphthalene green	1520	93000
Xanthenes		
Rhodamine 6G	940	6000
Rhodamine B extra	1250	22000
Fluorescein	2140	40000
Sulforhodamine B	1590	73000
Eosine A	2330	61000
Eosine S	1950	49000
Phloxine	1840	64000
Rose bengale	1080	>100000
Azines		
Neutral red	1400	46000
Phenosafranine	2200	88000
Pinacryptol green	1900	62000
Selestine blue	1720	>100000
Acridines		
Acridine yellow	1840	76000
Acridine orange	1680	81000
Pinacryptol yellow	2080	>100000
Thiazines		
Methylene blue	1400	1500
New methylene blue	1340	14000
Cyanines		
Garocyanine	1800	>100000
Chinolin blue	1920	67000
Pinacyanole	450	>100000
Azo dyes		
Oill red B	1640	>100000
Chrom blue black RC	2080	54000
Butter yellow	1840	41000
Fast light yellow G	1680	74000

In the case of sensitization on poly-*N*-vinylcarbazole, methylene blue is a little less sensitive than crystal violet. It is not evident why a large difference occurs between methylene blue and new methylene blue, because the two chemical formulas are very similar to each other. Methylene blue, rhodamine 6G, and victoria pure blue are all cationic dyes. The empirical tendency for the effective dyes to be cationics in the dye sensitization of poly-*N*-vinylcarbazole may also be applied in the case of polyacenaphthylene. Methylene blue, a thiazine dye, is known as a desensitizer in the silver

TABLE II. SENSITIZATIONS BY LEWIS ACIDS

	V_0, V.	$E_{1/2}$ lux.sec.
Acids and acid anhydrides		
Acetic acid	1535	>100000
Monochloroacetic acid	1550	>100000
Dichloroacetic acid	1040	>100000
Trichloroacetic acid	1340	11000
Monobromoacetic acid	1020	>100000
Tribromoacetic acid	1360	21000
Phenol	1245	>100000
p-Nitrophenol	1000	6000
Picric acid	1320	6000
Hydroquinone	1380	27000
Tetrachlorophthalic acid	960	7000
Tetrachlorophthalic anhydride	1310	7000
Benzoic acid	1500	82000
2, 4, 6-Trinitrobenzoic acid	1350	4000
Telephthalic chloride	1070	82000
Phthalic anhydride	1500	75000
Cinnamic acid	1630	80000
Acetanilide	1520	>100000
Oxalic acid	1120	92000
Succinic anhydride	1350	>100000
Maleic acid	1190	60000
Maleic anhydride	830	56000
Fumalic acid	1110	>100000
o-Toluic acid	1535	>100000
p-Aminobenzoic acid	1400	>100000
Aldehydes and Ketones		
p-Hydroxybenzaldehde	1480	>100000
2, 4-Dichlorobenzaldehyde	1480	>100000
p-Nitrobenzaldehyde	1560	98000
p-Dimethylaminobenzaldehyde	1510	>100000
Bromal	1400	>100000
o-Nitrobenzaldehyde	1535	>100000
Acetophenone	1680	>100000
Benzophenone	1550	>100000
Benzil	1480	>100000
Benzoin	1610	>100000
Quinones		
α-Naphthoquinone	850	18500
2, 3-Dichloronaphthoquinone	1090	1400
1-Nitoroanthraquinone	1420	1200
2, 6-Dichloro-*p*-benzoquinone	1390	4000
2-Chloroanthraquinone	1390	1900
2-Methylanthraquinone	1110	11000
p-Benzoquinone	1320	36000
p-Chloranil	1520	1800
Anthraquinone	1210	8800
1, 5-Dichloroanthraquinone	1100	1500
Anthraquinone-2-carboxilic acid	970	4000
Benzanthron	1470	>100000
α-Benzanthraquinone	1600	5000
1-Aminoanthraquinone	1330	>100000
2-Aminoanthraquinone	350	>100000
1, 4-Diaminoanthraquinone	950	>100000
Alizarine	1350	>100000
Quinizarine	1670	4100
Others		
5-Nitroacenaphthylene	1535	>100000
Trinitrobenzene	1170	2400

halide emulsions. This dye has positive effects, and cyanine dyes which are good sensitizers for the silver halides have no effect on the polymeric donor-type photoconductors.

Effective Dye Concentration.—In Fig. 1, a relation between the photosensitivity and the doping concentration of methylene blue is presented. In view of the accuracy of measuring, it can be said that the optimum dye concentration range is 0.03—0.1%. As the dye concentration increases, the dark decay rate increases as a result of a decrease in the dark resistivity.

Lewis Acid Sensitization.—The pure polyacenaphthylene showed an $E_{1/2}$ value of 1.6×10^5—1.8×10^5 lux. sec. and a V_0 value of 1400—1600 V. The dark decay rate was about 5 times that of poly-*N*-vinylcarbazole. These results imply that polyacenaphthylene has a lower value in the dark resistivity and a higher value in the light resistivity.*[2]

From Table II, it can be said that quinone derivatives are effective. 1-Nitroanthraquinone, 2, 3-dichloronaphthoquinone, 1, 5-dichloroanthraquinone, chloranil, and 2-chloroanthraquinone, which are strongly electron-attractive, show high sensitizabilities in white light without dye. This shows that the clear formation of a charge transfer complex is a favorable method for the sensitization when an effective dye is not used. The $E_{1/2}$ values of 1-nitroanthraquinone (1.2×10^3 lux. sec.) and 2, 3-dichloroanthraquinone (1.4×10^3 lux. sec.) are comparable with that of methylene blue (1.5×10^3 lux. sec.).

The Combined Effect of a Dye and a Strong Acid.—It has already been found that poly-*N*-vinylcarbazole was sensitized very highly with a cationic dye and a strong acid. Such a combined effect with a dye and acid might also be expected in the case of polyacenaphthylene. A compounded system of methylene blue (0.05%)+2, 4, 6-trinitrobenzoic acid (1%) shows 250 lux. sec., while a system of methylene blue (0.05%)+1-nitroanthraquinone (10%) or methylene blue (0.05%) + chloranil (10%) shows 1.3×10^3 or 2.5×10^3 lux. sec. respectively (see Fig. 2). Thus, an amplified

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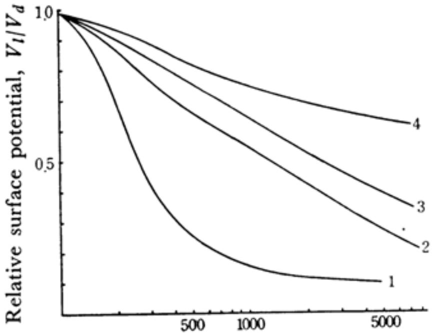
*[2] The $E_{1/2}$ value of pure poly-*N*-vinylcarbazole was found to be about 4000 lux.sec.



Exposure by time scale method, lux.sec.

Fig. 2. Electrophotographic characteristic curves of some sensitized polyacenaphthylene: 1, doped with 0.05% of methylene blue and 1% of 2,4,6-trinitrobenzoic acid; 2, doped with 0.05% of methylene blue and 10% of 1-nitroanthraquinone; 3, doped with 0.05% of methylene blue and 10% of chloranil; 4, doped with 0.05% of methylene blue and 10% of 2,3-dichloronaphthoquinone.

effect by using a dye and an acid is also to be seen in the sensitization of polyacenaphthylene.

From the view point of practical use in electrophotography, only methylene blue is found to be a significant dye.

Conclusion

The sensitized polyacenaphthylene with 0.05% of methylene blue and 1% of 2, 4, 6-trinitrobenzoic acid shows 250 lux. sec. in sensitometry with a half decay exposure. Nitrated polyacenaphthylene, which has an optimum degree of nitration (20—40 mol. %),[6] shows about 2×10^3 lux.sec. The methylene blue-sensitized sample of the nitrated derivative was found to be 550 lux. sec., which is about twice the foregoing system of polyacenaphthylene. From these results, the nitration is not likely to be a practical method for preparing elctrophotographic-sensitive material.

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[6] K. Morimoto and A. Inami, *J. Chem. Soc. Japan, Ind. Chem. Sect.* (*Kogyo Kagaku Zasshi*), **67**, 232 (1964).