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SYNTHESIS OF PANCHROMATIC PHOTOSENSITIZING DYES
Part II. Literature Survey

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Air Force Systems Command
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FOREWORD

This survey was prepared by Monsanto Research Corporation, Boston Laboratory, Everett, Massachusetts, under USAF Contract No. AF 33(657)-11430. The contract was initiated under Project No. 6272, Task No. 627204. The work was administered under the direction of the Air Force Avionics Laboratory, Research and Technology Division; Mr. James R. Pecqueux was project engineer.

This survey was prepared during the contract period from 1 April 1963 to 31 March 1964.

Dr. John S. Driscoll was Project Leader for Monsanto Research Corporation.

ABSTRACT

A critical, abstracted literature survey has been conducted in several areas pertaining to dye sensitized photoreactions with photographic applications. Silver halide sensitizers are covered during the 1961-1962 period. A 1949-1962 thionine dye survey is included.

This report has been reviewed and is approved.

James R. Pecqueux

James R. Pecqueux
Project Engineer
Photographic Branch
Reconnaissance Division
AF Avionics Laboratory

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I. INTRODUCTION

A limited literature survey has been conducted in several areas pertaining to dye sensitized photo-reactions with photographic applications. The areas covered include silver halide, photopolymerization, and free radical photographic sensitized reactions. The survey is critical, not comprehensive.

Because of the large number of patent references relating to silver halide sensitization, the early literature in this area is covered by background review articles. Dye sensitized photopolymerization and free radical photographic chemistry are much newer research areas with correspondingly fewer literature data available.

One-half the total number of silver halide sensitizer references obtained from Chemical Abstracts for the period 1961-1963 have been abstracted and are contained in this report. The remainder will be abstracted and reported during 1964 on Contract AF 33(615)-1343. A critical thionine dye literature survey (Chemical Abstracts 1949-1962) is complete in this report.

The following abbreviations are used:

λ_a = absorption maximum wavelength in millimicrons

λ_s = sensitization maximum wavelength in millimicrons

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II. BACKGROUND LITERATURE

A. SILVER HALIDE SENSITIZERS

1. "The Cyanine Dyes"

   F. M. Hamer, Quart. Rev., 4, 327 (1950).
   An excellent general review of the synthesis and properties of cyanine dyes used in photographic processes. 234 references.

2. "The Cyanine and Related Dyes"

   G. W. Anderson in Chemistry of Carbon Compounds, E. H. Rodd, Ed., Vol. 4B, Elsevier, Amsterdam, 1959, 1053.
   A very good general review containing 164 references.

3. "Sensitizing and Desensitizing Dyes"

   L. G. S. Brooker in The Theory of the Photographic Process, 2nd Ed., C. E. K. Mees, Ed., Macmillan, N. Y., 1954, 371.
   A good first introduction to the subject. The book also contains a valuable chapter on "The Mechanism of Optical Sensitizing".

4. "Cyanine Dyes"

   R. C. Elderfield in Heterocyclic Compounds, Vol. 4, R. C. Elderfield, Ed., Wiley, N. Y., 1952, 94.
   A brief review with emphasis on quinoline cyanines.

5. "Cyanines"

   H. A. Lubs, The Chemistry of Synthetic Dyes and Pigments, Reinhold, N. Y., 1955, 251.
   A very brief historical review with 22 references.

6. "Some Recent Developments in the Chemistry of Photographic Sensitizing Dyes"

   L. G. S. Brooker, International Congress of Pure and Applied Chemistry, June 1955 supplement to Experientia, 229.
   A review of Brooker's early 1950 work with emphasis on the correlation of structure with absorption frequency.

7. "Progress in the Field of Sensitizing Dyes for Photographic Halogen-Silver Emulsions"

   K. Kainrath, Angew. Chem., 60, 36 (1948).
   A discussion of the work of the early 1940's with 47 patent references.

8. "Sensitization of Photographic Films by Dyes"

H. Wolff, *Fortschritte der Chemischen Forshung*, 3, 503 (1955).
A review of structure and mechanism in sensitization in terms of solid-state physics.

9. "The Chemistry of Photographic Sensitizing Dyestuffs"

J. O. Kendall, *Chem. and Ind.*, *1950*, 121.
A general talk given before the Chemical Society in 1949. Not much specific detail.

10. "Organic Dyes"

H. W. Grimmel in *Organic Chemistry*, H. Gilman, Ed., Vol. III, Wiley, N. Y., 1953, 243.
A very short, incomplete review of the cyanines.

11. "The Cyanine Dyes"

M. Q. Doja, *Chem. Rev.*, *11*, 273 (1932).
A review of the preparation of the relatively simple compounds of the early literature.

12. "Cyanine Dyes"

G. H. Keyes and E. J. Van Lare in *Encyclopedia of Chemical Technology*, R. E. Kirk and D. F. Othmer, Eds., Vol. 4, Interscience, N. Y., 1949, 742.
A brief review of representative cyanines up to 1948 with 62 references.

13. "Steric Hindrance to Planarity in Dye Molecules"

L. G. S. Brooker, F. L. White, R. H. Sprague, S. G. Dent and G. Van Zandt, *Chem. Rev.*, *41*, 325 (1947).
An explanation of the effect of steric non-planarity on the visible absorption spectrum of dyes - the Brunings-Corwin Effect.

14. "Color and Constitution"

L. G. S. Brooker, et al., *J. Am. Chem. Soc.*, *62*, 1116 (1940), *63*, 3192, 3203, 3214 (1941), *64*, 199 (1942), *67*, 1869, 1875, 1889 (1945).
An excellent series of papers relating to the effects of structure on color. Experimental details for many complex cyanine dyes are given.

15. "The Effect of Non-Coplanarity on the Light Absorption of Cyanine Dyes"

M. J. S. Dewar in Steric Effects in Conjugated Systems, G. W. Gray, Ed., Academic Press, N. Y., 1958, 46. A critical review of the resonance explanation of the Brunings-Corwin effect is given. The author offers an explanation based on molecular orbital theory that is claimed to resolve some of the difficulties associated with the resonance explanation.

B. PHOTOPOLYMERIZATION SENSITIZERS

1. "Sensitizers of Photopolymerization"

G. Delzenne, Ind. chim. belge, 24, 739 (1959).
A good review of the title subject. Although dye sensitizers are treated, the emphasis is on U.V. absorbers. 143 references.

III. CURRENT PHOTOSENSITIZER LITERATURE

A. SILVER HALIDE SENSITIZERS

1. "6'-Aminoselena-2'-cyanines and its sensitizing properties"

K. Meyer and K. H. Bauer, Z. wiss. Phot., 54, 171 (1960).
C.A., 55, 10157e (1961).
Strong sensitizer. λ_s 545. Synthesis given.

2. "Hemicyanine dyes"

G. F. Duffin and J. D. Kendall, Brit. 850,976, Oct. 12, 1960.
C.A., 55, 10161e (1961).
About 20 derivatives of substituted hydrazines prepared.
λ_s about 500.

3. "Aza cyano methine dyes"

M. Coenen, Ger. 1,063,732, Aug. 20, 1959. C.A., 55, 10162e (1961).
Seven substituted cyanoethylenes described. Colors of neutral compounds and anions given.

4. "Indolene compounds"

G. E. Ficken and J. D. Kendall, Brit. 845,586, Aug. 24, 1960.
C.A., 55, 10162h (1961).
A cyanine dye intermediate.

5. "Improvements in indoline cyanine dyes"

G. E. Ficken and J. D. Kendall, Brit. 845,587, Aug. 24, 1960. C.A., 55, 10162i (1961). Cyanine intermediates relating to preceding and following references.

6. "Trinuclear cyanine dyes"

G. E. Ficken, D. J. Fry and J. D. Kendall, Brit. 845,588, Aug. 24, 1960. C.A., 55, 10163d (1961). Unsymmetrical indole trinuclear cyanines prepared. λ_s 635, 620 and 585.

7. "Cyanine dyes"

M. Coenen and O. Weissel, Ger. 1,070,316, Dec. 3, 1959. C.A., 55, 10164a (1961). Indole trimethine cyanines prepared from aldehydes and heterocyclic methylenes.

8. "Methine dyes"

J. D. Kendall, H. R. Waddington and G. F. Duffin, Brit. 856,068, Dec. 14, 1960. C.A., 55, 10164e (1961). Unsymmetrical mono- and trimethine coumarin cyanines described. λ_a 425-580.

9. "Cyanine dyes"

M. Coenen and O. Weissel, Ger. 1,073,662, Jan. 21, 1960. C.A., 55, 11152b (1961). Indole cyanine dyes prepared similar to those in ref. 7. Claimed to be valuable sensitizers.

10. "Supersensitization of cyanine dyes"

J. E. Jones, U.S. 2,972,539, Feb. 21, 1961. C.A., 55, 11152h (1961). Supersensitization is obtained from mixtures of merocyanines and carbocyanines. Synthesis of methine-substituted thiacarbocyanines described.

11. "*p*-(2-Pyrazolin-1-yl)styryl dyes"

A. F. Plue, U.S. 2,974,141, Mar. 7, 1961. C.A., 55, 11153c (1961). Six cyanine-type dyes prepared consisting of indole and pyrazole bases connected by a *p*-styryl group.

12. "Dicyanopolymethine dyes having no salt structure"

W. Franke and P. Kainrath, Ger. 1,056,307, April 30, 1959.
C.A., 55, 12121f (1961).
A number of benzothiazole cyanohexamethine anilines prepared.
λ_a 675, 685, 515, 673, 520, 670, 695, 590 and 669.

13. "Symmetrical and unsymmetrical betainecarbocyanine dyes"

H. V. Rintelen, Ger. 1,072,765, Jan. 7, 1960. C.A., 55, 12122a (1961).
Carbocyanine N-sulfoalkyl inner salts prepared. λ_s 648, 639, 652, 663, 597, 610, 637 and 615.

14. "Photographic supersensitizers"

J. E. Jones, U.S. 2,977,229, Mar. 28, 1961. C.A., 55, 14136d (1961).
A number of simple cyanines and merocyanines useful as supersensitizers for Ag halide emulsions sensitized with simple cyanines are described. Sulfoalkyl inner salts described (see ref. 13).

15. "Cyanine dyes"

K. Küffner, Ger. 1,073,133, Jan. 14, 1960. C.A., 55, 14138f (1961).
Simple merocyanines and carbocyanines of tetrahydropyridine derivatives described. λ_s 540, 470, 545. Dyes can be easily removed from plates by solution.

16. "Aza cyano methine dyes"

M. Coenen, Ger. 1,067,155, Oct. 15, 1959. C.A., 55, 16236i (1961).
Three straight-chain polycyanoazadecamethine compounds described.

17. "Pyrrolenine dyes"

D. J. Fry, B. A. Lea and J. D. Kendall, U.S. 2,979,501, April 11, 1961. C.A., 55, 16237b (1961).
Isomeric pyrrole-merocyanine type dyes are prepared with λ_s 550, 450, 530, 535, 480 and 540.

18. "Synthesis of dicarbocyanines by cleavage of the pyrylium ring in pyrylocyanines"

A. I. Tolmachev, Zhur. Obschei Khim. 30, 2892 (1960).
C.A., 55, 17313g (1961).
A ring-opening reaction of cationic oxygen heterocycles converts a monomethine to a pentamethine. λ_a 640-685.

19. "Dicarbocyanines"

D. J. Fry and J. D. Kendall, Brit. 859,452, Jan. 25, 1961. C.A., 55, 17316g (1961). Aminopyrimidines are cleaved with active methyl heterocycles to give symmetrical pentamethinecyanines useful as optical sensitizers.

20. "Sensitization of silver halide emulsions"

G. Bach, Ger. 1,063,028, Aug. 6, 1959. C.A., 55, 17321f (1961). Bulky heterocyclic substituents on carbocyanine dyes increase red sensitivity without undesirable side effects. λ_s 580, 560-5, 600-5.

21. "Cyanine dyes"

A. B. Lal, Chem. Ber., 94, 1723 (1961). C.A., 55, 18399e (1961). Styryl cinnoline compounds prepared as well as unsymmetrical cinnoline trimethinecyanine dyes, which are blue.

22. "Synthesis of cyanine dyes by the condensation of p-diethylaminobenzaldehyde with appropriate heterocyclic compounds IX"

M. Q. Doja and A. K. Sinha, J. Indian Chem. Soc., 37, 146 (1960). C.A., 55, 20438d (1961). Four new styryl compounds of 5- and 6-substituted quinaldine ethiodides were prepared. Solutions were violet.

23. "Photographic sensitizers"

J. D. Kendall, H. R. J. Waddington and G. F. Duffin, Brit. 867,592, May 10, 1961. C.A., 55, 21927b (1961). 3-Heterocyclic substituted coumarins sensitize AgCl emulsions with λ_s 480, 490, 460, 470 and 450.

24. "Merocyanine photographic sensitizers"

P. D. Collet, Fr. 1,242,962, Jan. 11, 1961. C.A., 55, 21927h (1961). Pyridylidene merocyanines, similar to the types claimed to be supersensitizers (see ref. 14) were prepared.

25. "Photographic sensitizers"

J. Götze, Ger. 1,051,115, Feb. 19, 1959. C.A., 55, 21928f (1961). Substituted benzoxazole cyanines sensitize photographic emulsions with λ_s 542, 600, 570, 590, 505, 560, 565 and 720.

26. "Pentamethinecyanine dyes"

G. E. Ficken and J. D. Kendall, Brit. Patent 867,403, May 10, 1961. C.A., 55, 21929g (1961).
2-Chloro-3,3-dimethylinoline is used to prepare symmetrical pentamethine cyanines with λ_s 585, 610, and 700.

27. "Cyanosubstituted cyanine dyes"

W. Franke and P. Kainrath, Ger. Patent 1,060,528, July 2, 1959. C.A., 55, 21930e (1961).
Non-salt, cyanine dyes synthesized from heterocyclic pyruvic acid oximes. λ_s 505-640.

28. "2-Methyl-6-(2-carbamoylethoxy)benzothiazoles and their quaternary salts"

L. Horwitz and C. B. Roth, U. S. Patent 2,984,667, May 16, 1961. C.A., 55, 21930i (1961).
Carbamoylthiopseudocyanines are synthesized in a number of steps to yield sensitizers with λ_s 480-645.

29. "Hydroxypyrrolinemethine dyes"

D. J. Fry, B. A. Lea and J. D. Kendall, U. S. Patent 2,984,663, May 16, 1961. C.A., 55, 21931h (1961).
A highly substituted pyrrole is condensed with active methyl or methylene compounds to give AgCl-AgBr sensitizers with λ_s 450-630.

30. "Sensitizing dyes"

L. Berlin and H. Hamal, Ger. Patent 1,098,653, Feb. 2, 1961. C.A., 55, 23135 (1961).
Complex polyheteronuclear benzothiazoles sensitize silver halide emulsions with λ_s 540-630. A quinolylidene rhodanine was prepared that is similar to previously mentioned supersensitizers (ref. 14).

31. "Dicarbocyanine dyes"

R. C. Wilson, Ger. Patent 1,090,801, Oct. 13, 1960. C.A., 55, 24336g (1961).
The use of acetals of malondialdehyde rather than dianils is claimed to give pure dicarbocyanine products.

32. "Pentamethinecyanines"

D. J. Fry, J. D. Kendall and A. J. Morgan, Brit. Patent, 870,633, June 14, 1961. C.A., 55, 24336i (1961).
A large number of highly conjugated dyes prepared with a trimethine chain inserted by quaternary pyrimidine ring opening. All compounds have absorption near 700 mμ. Most are feeble sensitizers.

33. "Methine dyes"

G. E. Ficken and J. D. Kendall, Brit. Patent 870,753, June 21, 1961. C.A., 55, 25560a (1961).
The 3,4-diazaindene ring system (fused pyridine and pyrroline rings) utilized in unsymmetrical mono- and trimethine cyanine systems. Many prepared; most are sensitizers with λ_s 500-600.

34. "The color of organic compounds. IX. Merocyanines derived from 2-hydroxythiazoles and thiazole-2-thiols".

E. B. Knott, J. Chem. Soc., 1960, 4244, C.A., 26801b (1961)
Merocyanines and cyanines derived from keto forms of the title compounds were synthesized. Unsymmetrical di- and trinuclear compounds included. λ_a in article but not in abstract.

35. "Hemioxonol dyes containing a carbocyclic nucleus"

E. J. Van Lare, U. S. Patent 2,956,881, Oct. 18, 1960. C.A., 55, 6221h (1961).
Thiobarbituric acid dyes synthesized in very poor yields. λ_s 530-635.

36. "Hemicyanine dyes"

G. F. Duffin and J. D. Kendall, Brit. Patent 849,741, Sept. 28, 1960. C.A., 55, 6222h (1961).
Acetylated hydrazino derivatives of heterocyclic systems were found to sensitize emulsions with λ_s 440-480.

37. "Polymethine dyes containing a 4-(hydroxymethyl)-2-thiazoline or oxazoline nucleus"

J. Nys and J. Libeer, U. S. Patent 2,954,376, Sept. 27, 1960. C.A., 55, 7114i (1961).
4,4-Substituted title compounds are described. λ_a given but no mention of λ_s or other sensitizing properties.

38. "Supersensitization of complex cyanine dyes"

J. E. Jones, U. S. Patent 2,947,630, Aug. 2, 1960. C.A., 55, 7116b (1961).
Supersensitization is claimed with certain unspecified sulfonated polynuclear aromatics and a large number of specified polynuclear heterocyclic cyanines. No λ_s data.

39. "Cyanine dyes"

J. D. Kendall and G. F. Duffin, Brit. Patent 835,275, May 18, 1960. C.A., 55, 187e (1961).
Non-ionic sensitizers are prepared by the reaction of alkyl- and aryloxy acetic esters with standard heterocyclic systems in the presence of base. λ_s 430-535.

40. "Supersensitized photographic emulsions"

Kodak, Soc. anon., Belg. Patent 588,862, April 15, 1960. C.A., 55, 12511 (1961).
This patent gives quantitative data on the relative sensitivity, gamma, and fogging values for certain cyanines supersensitized with the pyridylidine rhodanine compounds described in a U. S. patent (ref. 14).

41. "Dicarbocyanine dyes"

R. C. Wilson, U. S. Patent 2,951,841, Sept. 6, 1960. C.A., 55, 2320f (1961).
The triethylmethyl acetal of malondialdehyde reacts with quaternary salts of the usual heterocyclic bases such as benzothiazole, benzoselenazole in the presence of pyridine to give dicarbocyanine dyes. λ_a 655.

42. "Azamerodicarbocyanine dyes"

Kodak anon., Belg. Patent 587,287, Feb. 29, 1960. C.A., 55, 2320h (1961).
Dicarbomerocyanine dyes were prepared in which the methine group $(-\overset{H}{C}=)$ in the α position was replaced by an imine group $(=N-)$. These were prepared from the usual keto methylene heterocyclic nuclei bearing an aminomethylene group adjacent to the keto function and the anilinovinyl or acetylanilinovinyl derivatives of quaternary heterocyclic bases.

43. "The phosphonines, a new class of spectral sensitizers in photography".

A. Van Dormael, J. Nys and H. Depoorter, Sci. et inds. phot., 31, 389 (1960). C.A., 55, 4210d (1961).
Polymethine dyes containing the $>C=P<$ as the terminal groups of the unsaturated chain or in conjunction with N or O terminal groups are useful as spectral sensitizers.

44. "Photosensitive materials for reproduction purposes".

O. Süs, Ger. Patent 1,047,622, Dec. 24, 1958. C.A., 55, 4214d (1961).
Light-sensitive materials containing the diazo compounds derived from 1,2-benzo- or naphthoquinones linked through a sulfophenyl group to an imidazole nucleus were prepared.

45. "Supersensitization of photographic emulsions"

J. Nys, Ger. Patent 1,013,167, Aug. 1, 1957. C.A., 55, 3253f (1961).
Trinuclear cyanines were found to increase the red sensitivity of color films. λ_s 650-710.

46. "Cyanine dyes from 2-methyl-4-(1-azulenyl)thiazole"

J. Brunken and E. J. Poppe, Chem. Ber., 93, 2572 (1960).
C.A., 55, 4208i (1961).
2-Methyl-4-(1-azulenyl)thiazole condensed with usual heterocyclic derivatives to give trimethine merocyanines with poor sensitizing properties.

47. "Sensitizing dyes"

G. F. Duffin, J. D. Kendall and H.R.J. Waddington, Brit. Patent 839,020, June 29, 1960. C.A., 55, 2322i (1961).
Triazinopyridazine trimethine cyanines sensitize silver chloride emulsions with λ_a 490-560.

48. "Photographic sensitizers"

M. S. Magson, Brit. Patent 841,119, July 13, 1960. C.A., 55, 2323h (1961).
Non-migratory sensitizers, stable to color formers are claimed from the synthesis of N-carboxyethyl benzoxazole trimethines. λ_a 500.

49. "Cyanine dyes"

H.R.J. Waddington, G. F. Duffin and J. D. Kendall, Brit. Patent 848,016, Sept. 14, 1960. C.A., 55, 5205a (1961).
Cyanine dyes containing the 2,4,4,6-tetramethyl-4H-1,3-thiazine nucleus and the usual heterocyclic bases were prepared. λ_s 505.

50. "Sensitization of red-sensitive silver halide emulsions".

J. Nys, Ger. Patent 1,024,800, Feb. 20, 1958. C.A., 55, 4214g (1961).
Trinuclear dyes with both a cyanine and merocyanine structure were prepared incorporating benzothiazole, rhodanine and diphenylthiazole nuclei. λ_s 640-665.

51. "Photographic sensitizers"

D. J. Beavers, C. V. Wilson and J. L. Graham, U.S. Patent 2,940,855, June 14, 1960. U.S. Patent 2,944,898, July 12, 1960. C.A., 55, 1253b (1961).
Long-chain (22 carbon atoms) quaternary ammonium salts are claimed to sensitize emulsions with no increase in fog or loss of speed.

52. "Carbocyanine dyes containing benzimidazole rings"

J. Ciernik, Chem. listy, 55, 44 (1961). C.A., 55, 6217 (1961). A review discussing the suitability of benzimidazole cyanine dyes for color photography, the relationships determining optical and photographic properties, the effect of substituents on absorption and sensitization max., and the preparation of carbocyanine imidazole dyes with 69 references.

53. "Holopolar cyanine dyes"

L.G.S. Brooker and F. L. White, U. S. Patent 2,955,939, Oct. 11, 1960. C.A., 55, 6220b (1961). A series of heterocyclic cyclopentylidene barbituric acids were shown to have λ_s 520-770.

54. "Dimethine dyes"

D.J. Fry and B. A. Lea, Brit. Patent 846,298, Aug. 31, 1960. C.A., 55, 7117f (1961). Dimethine merocyanine dyes substituted on the methine chain by alkylcarboxylic acid groups were prepared with λ_s 530-630.

55. "Holopolar dyes derived from 3-indazolinone"

F. G. Webster and L.G.S. Brooker, U. S. Patent 2,961,317, Nov. 22, 1960. C.A., 55, 6221b (1961). Polymethine dyes containing the usual heterocyclic rings linked to the 3-indazolinone nucleus were prepared with λ_s 510-590.

56. "Cyanine dyes from thienylbenzoxazole as photographic sensitizers"

J. Goetze, U.S. Patent 3,044,875, July 17, 1962. C.A., 57, 13339d (1962). Dyes of the cyanine and merocyanine class were prepared from benzoxazole with an α-thienyl substituent in the 5-position. λ_s 505-630.

57. "Polymethine dyes"

Gevaert, Belg. Patent 615,549, April 13, 1962. C.A., 57, 14623f (1962). Cyanine and merocyanine dyes were prepared containing at least one benzimidazole ring in which the benzene ring carries at least one amino group and one halogen atom. λ_a 514-529.

58. "Photographic cyanine dyes containing the benzisoxazole ring"

E. B. Rauch, Belg. Patent 615,195, April 13, 1962. C.A., 57, 16045 (1962). Merocyanines, carbo- and dicarbocyanines containing the benzisoxazole ring were prepared with λ_a 480-600.

59. "Merocyanine sensitizing dyes"

E. B. Knott, U. S. Patent 3,033,681, May 8, 1962. C.A., 57, 16046b (1962).
Merocyanine dyes containing the 2',3'-dihydro-5-oxobenzothiazolo[2',3'-2,1]glyoxaline-hydrochloride nucleus were prepared. λ_a 510-580.

60. "Polymethine dyes"

Gevaert, Belg. Pat. 615,547, April 13, 1962. C.A., 57, 16049 (1962).
Cyanine and merocyanine dyes were prepared which contain at least one benzimidazole ring system substituted at the 5 and 6 position with a halogen atom. λ_a 408-518.

61. "Cyanine dyes with unsaturated substituents"

L. N. Tyurina, M. A. Al'perovich and I. K. Ushenko, Zh. Obshch. Khim. 32, 70 (1962). C.A., 57, 12663 (1962).
Merocyanine dyes containing the benzothiazole nucleus substituted at the 6 position with a styryl group were prepared. λ_a 531-618.

62. "Sensitization of photographic layers containing azo dyes".

H. Bruengger and H. Boehl, Ger. Patent 1,083,124, June 9, 1960. C.A., 56, 12462 (1962).
Cyanine dyes with a betaine structure involving the hetero atom were prepared.

63. "Phenothiazine styryl sensitizers"

L. P. Roosens, Belg. Patent 569,[illegible]03, Nov. 2, 1963. C.A., 56, 13704 (1962).
Styryl dyes containing the phenothiazine nucleus and the 5 oxo-pyrazolinylidene nucleus were prepared, λ_a 430-680.

64. "Polymethine dyes"

J. Nys and H. Depoorter, Belg. Patent 568,759, Oct. 16, 1948. C.A., 56, 13703 (1962).
Esters of alcohols containing a sulfo group were used to prepare methine dyes in which the heterocyclic nitrogen atom was substituted by the esters prepared. Both sodium salts and betaine forms were used, λ_a 470-650.

65. "Sensitization of silver halide emulsions containing color couplers".

G. Bach and G. Beuleg, Ger. Patent 1,113,873, Jan. 17, 1959. C.A., 56, 8220 (1962).
Trimethine cyanine dyes with an ethyl group on the meso carbon atom and containing benzoxazole and benzoselenazole nuclei substituted in the 5 position with methoxyl groups were prepared.

66. "Sensitization of silver halide emulsions"

G. Bach, East Ger. Patent 19,683, Aug. 18, 1960. *C.A.*, *56*, 11113 (1962).
Cyanine and styryl dyes were prepared in which the heterocyclic nucleus was substituted in the 5 position with a similar heterocyclic nucleus, λ_s 560-605.

67. "Methine dyes"

A. G. Farben, Brit. Patent 886,091, Jan. 3, 1962. *C.A.*, *56*, 13707 (1962).
Merocyanine dyes containing the pyrazoline ring were prepared from 4-formyl-3-methyl-1-phenyl-5-pyrazolone and various keto methylene heterocycles.

68. "Polymethine dyes"

J. Nys and H. Depoorter, Belg. Patent 569,130, Nov. 2, 1958. *C.A.*, *56*, 13705 (1962).
Various cyanine dyes, substituted at the heterocyclic nitrogen atom with an alkyl group containing at least one SO_2 or CO group linked to an NH group are prepared, λ_s 480-730.

69. "Polymethine dyes"

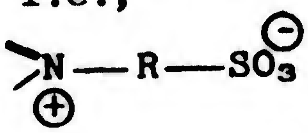
G. E. Ficken and J. D. Kendall, Brit. Patent 874,809, Aug. 10, 1961. *C.A.*, *56*, 15077 (1962).
A number of merocyanine dyes containing the 3'-methylindolo-[2',1',2,3]thiazolidin-4-one nucleus as the keto methylene group were prepared, λ_s 485-560.

70. "Cyanine and merocyanine dyes"

J. D. Kendall, G. F. Duffin and H.R.J. Waddington, Brit. Patent 862,825, March 15, 1961. *C.A.*, *56*, 15076 (1962).
Mono and trimethinecyanine and merocyanine dyes containing the 1,5,6-triazaindolizine group were synthesized.

71. "Betaine sulfate carbocyanine dyes"

G. Bach and W. Feigner, East Ger. Patent 20,781, Feb. 6, 1961. *C.A.*, *56*, 15080 (1962).
A number of carbocyanine dyes were prepared with the nitrogen atom of the heterocyclic nucleus bearing an alkyl sulfato group and possessing a betaine structure, i.e.,



$$>\underset{\oplus}{N}-R-SO_3^{\ominus}$$

72. "Benzimidocarbocyanine sensitizers"

G. Bach, Ger. Patent 1,121,925, Jan. 11, 1962. C.A., 56, 15078 (1962).
A number of cyanine dyes containing the benzimido nucleus substituted in the benzene ring by halogen and cyano groupswere prepared, λ_s 530-560.

73. "Sensitized silver halide emulsions"

D. M. Burness, K. C. Kennard and B. C. Cossar, Ger. Patent 1,125,277, March 8, 1962. C.A., 57, 3015a (1962).
Nonpolymeric bis-quarternary salts of disulfones were prepared and claimed as sensitizers.

74. "Cyanine dyes"

H. Larive and R. J. Wennilauler, Fr. Patent 1,274,963, Feb. 28, 1962. C.A., 57, 3015h (1962).
Monomethine cyanine and merocyanine dyes were prepared containing the usual heterocyclic nuclei.

75. "Silver halide photographic emulsions containing linear polyamine sensitizing agents".

V. C. Chamber, Jr., and A. E. Oberth, U.S. Patent 3,026,203, March 20, 1962. C.A., 57, 1790 (1962).
Sensitivity of photographic emulsions is increased by the addition of linear polyamines in which all the amino groups are secondary and are linked by 2- and 3-carbon chains.

76. "Cyanines for color photography"

Kodak Soc. Anon., Belg. Patent 607,696. C.A., 57, 332 (1962).
A number of sensitizing cyanine and merocyanine dyes were prepared in which the nitrogen atom of the methine chain was present as the dicyanomethylene group. λ_a 490-810.

77. "Polymethine dyes containing phosphorus"

A. van Dormael, J. Nys and H. Depoorter, Belg. Patent 583,922, Feb. 16, 1960. C.A., 57,331 (1962).
A number of cyanine dyes containing the triphenyl phosphine group conjugated with the usual heterocyclic nuclei were prepared from triphenyl phosphonium cyclopentadienylide. λ_s 425-640.

78. "Sensitization of photographic silver halide emulsions"

J. Nys and H. Depoorter, Ger. Patent 1,081,311, May 5, 1960. C.A., 57, 328g (1962).
A number of cyanine and merocyanine dyes were prepared in which the heterocyclic nitrogen was substituted with an organic group containing two or more of the following groups: $-SO_2-$, $>C=O$ or $-NH_2$. λ_s 480-660.

B. PHOTOPOLYMERIZATION SENSITIZERS

GENERAL

1. "Photopolymerization"

General Aniline and Film, Belg. Pat. 622,882, Sept. 26, 1962. Photopolymerization to images of a photopolymerizable monomer or monomer mixture is carried out for the production of printing plates having a suitably thick image and relatively high printing contrast.

2. "Photopolymerization of vinyl monomers by means of a radiation absorbing component in the presence of a diazonium compound"

S. Levinos, U. S. Patent 3,099,558, filed June 26, 1959. *Official Gazette*, U.S. Patent Office, July 30, 1963, 1217. A terminal olefin is polymerized by a U.V.-visible source in the presence of a diazonium catalyst sensitized by a dye (azo, cyanine, styryl, merocyanine, etc.).

3. "Photopolymerization of unsaturated organic compounds by means of radiation sensitive iron compounds as photoinitiators"

H. D. Evans and F.W.H. Mueller, U. S. Patent 3,101,270, filed April 27, 1959. *Official Gazette*, U.S. Patent Office, Aug. 20, 1963, 522.
The iron salt of an aliphatic acid is used to activate monomer polymerization through the decomposition of a peroxide.

THIONINE COMPOUNDS

1. "Oxygen production by illuminated chloroplasts suspended in solutions of oxidants".

A. S. Holt and C. S. French, *Arch. Biochem.*, 19, 368 (1949). *C.A.*, 43, 8009 (1949).
Thionine was photochemically decolorized in the presence of spinach chloroplasts.

2. "The photochemical reduction of thionine".

L. J. Heidt, *J. Chem. Ed.*, 26, 525 (1949). *C.A.*, 44, 1766g (1950). Details are given for a lecture demonstration based on the reversibility of the reaction:

$$\mathrm{Fe}^{+2} + \text{thionine (purple)} \underset{\text{dark}}{\overset{h\nu}{\rightleftharpoons}} \mathrm{Fe}^{+3} + \underset{\text{(colorless)}}{\text{reduced thionine}}$$

3. "Reversible polymerization and molecular aggregation".

L. Michaelis, J. Phys. and Colloid. Chem., 54, 1 (1950). C.A., 44, 3772a (1950).
Thionine was studied with regard to reversible polymerizations in the presence of nucleic acids and agar and deviations from Beer's Law.

4. "Reactions of the reduced form of chlorophyll".

A. A. Krasnovskiĭ and G. P. Brin, Doklady Akad. Nauk S.S.S.R., 73, 1239 (1950). C.A., 45, 3037i (1951).
Chlorophyll a and b were photochemically reduced by ascorbic acid and the rate of reoxidation with thionine (E = 0.062v) determined. The redox potential of the chlorophyll system was found to be ca. -0.35v.

5. "Becquerel's photovoltaic effect in the system thionine-thiosinamine.

E. Matijević, Arhiv Kem., 21, 1, 22 (1949). C.A., 45, 4141f, 4142b (1951).
The voltage produced when thionine was photoreduced in the presence of thiosinamine was studied as were the effects of the electrolyte on E.

6. "Photodynamic action of methylene blue on nicotine and its derivatives".

L. Weil and J. Maher, Arch. Biochem., 29, 241 (1950). C.A., 45, 4563e (1951).
Thionine was photoreduced at a specific visible wave-length by nicotine under anaerobic conditions. In the presence of O_2, the leuco-dye is reoxidized with probable H_2O_2 formation.

7. "The photochemical activity of $FeCl_4^-$ in alcohol as an oxidizing agent and as catalyst".

G. J. Brealey and N. Uri, J. Chem. Phys., 20, 257 (1952). C.A., 46, 7436f (1952).
$FeCl_4^-$ is shown to be a photocatalyst for the oxidation of ethanol by thionine.

8. "The metallic model of thionine and methylene blue. Analysis of a quantum theory of colored indicators".

S. Nikitine, J. chim. phys., 49, 175 (1952). C.A., 46, 8519i (1952).
The energy levels for thionine are calculated from spectral data with the aid of an equation which assumes that the π-electrons are in the form of a one dimensional electron gas. Decolorization of thionine during pH changes is regarded as an interruption of metallic resonance.

9. "Interpretation of the absorption spectra of certain classes of organic dyes".

S. Nikitine, <u>Gazz. chim. ital.</u>, <u>82</u>, 476 (1952). <u>C.A.</u>, <u>47</u>, 4738e (1953). Using the metal model theory (ref. 8), the positions and intensities of the absorption bands of thionine and methylene blue were calculated.

10. "Photobleaching and photorecovery of dyes".

G. Oster and N. Wotherspoon, <u>J. Chem. Phys.</u>, <u>22</u>, 157 (1954). <u>C.A.</u>, <u>48</u>, 4339h (1954).
Photobleaching of thionine occurs when ascorbic acid or phenylhydrazine is present. In the absence of oxygen, the color is not restored. $SnCl_2$ at pH >1.5 will photoreduce the dye, but at <1.5 reduction takes place in the dark.

11. "The photolysis of 3-indoleacetic acid".

L. Brauner, <u>Z. Botan.</u>, <u>41</u>, 291 (1953). <u>C.A.</u>, <u>48</u>, 5296a (1954). Thionine was found to be one of the better photo-oxidizing agents for the photolytic determination of 3-indoleacetic acid.

12. "The oxidation-reduction potential of several anthraquinones and vat dyes".

H. W. Meyer and W. D. Treadwell, <u>Helv. Chim. Acta</u>, <u>35</u>, 1444 (1952). <u>C.A.</u>, <u>48</u>, 7305b (1954).
The redox potentials of a number of dyes were measured as a function of pH.

13. "Chemical synthesis accomplished by x-rays and by other peroxidizing physical agents (ultraviolet and ultrasonic rays)".

J. Loiseleur, <u>Ann. inst. Pasteur</u>, <u>86</u>, 262 (1954). <u>C.A.</u>, <u>48</u>, 7074f (1954).
X-rays, ultrasound and uv light were used to synthesize thionine from phenolic compounds in the presence of O_2.

14. "Influence of acidity on the absorption spectra of vat dyes and the relation to oxidation-reduction potential".

H. W. Meyer and W. D. Treadwell, <u>Helv. Chim. Acta</u>, <u>35</u>, 1460 (1952). <u>C.A.</u>, <u>48</u>, 7433f (1954).
Spectra are discussed as a function of pH.

15. "Transfer of energy from thiazines to pinacyanol".

S. Rémy, <u>J. chim. phys.</u>, <u>51</u>, 139 (1954). <u>C.A.</u>, <u>48</u>, 13440c (1954).
The quantum efficiency of fluorescent <u>vs</u> non-fluorescent dyes on the decolorization of pinacyanol was studied. Non-fluorescent dyes had no effect.

16. "Spectrophotometric studies on the interaction of nucleic acids with aminoacridines and other basic dyes"

P.P.H. De Bruyn and N.H. Smith, Exptl. Cell Research, 7, 201 (1954). C.A., 49, 1112 f (1955).
Thionine and other dyes were found to form complexes with nucleic acids.

17. "Interaction between basic dyes and high molecular anions"

N. Mataga, J. Inst. Polytech., Osaka City University, 4C, 189 (1953). C.A., 49, 2868a (1955).
The influence of K polyvinyl sulfate and Na lauryl sulfate on the spectrum of thionine and other dyes was determined.

18. "Absorption spectra of thiazine dyes adsorbed on crystal surfaces"

N.E. Vedeneeva, Doklady Akad. Nauk S.S.S.R., 98, 585 (1954). C.A. 49, 4405b (1955).
The cations on the surface of a clay dyed by methylene blue change the absorption properties of the dye.

19. "Reversible photochemical process in the system thionine - phenyl - hydrazinesulfonate"

E. P. Kostrynkova, Ukrain. Khim. Zhur., 21, 54 (1955). C.A., 49, 12973 e (1955).
Light absorption was found to effect the equilibrium for the reaction between the title compounds. H atom transfer was shown to involve an increase in free energy.

20. "The nature of the composition of active centers in photocatalysis"

I.N. Barshchevskir and L.A. Nikolaev, Problemy Kinetiki i Kataliza, Akad. Nauk S.S.S.R., 8, 61 (1955). C.A., 50, 1434d (1956).
Heavy metal ions influence the ZnO catatyzed photoreduction of thionine by formaldehyde and other reducing agents.

21. "Photogalvanic effects in the system thionine - thiosinamine"

W. Hendrich, Rocsniki Chem., 29, 1149 (1955). C.A., 50, 91771 (1956).
The potential of the title system was found to be a function of pH and illumination. Illumination caused the reduction of thionine, the oxidation of thiosinamine and a ΔE of -310 mv.

22. "The sensitization mechanism of the internal photoeffects of silver and thallium iodides by organic dyes."

I.A. Akimov, Zhur, Fiz. Khim., 30, 1007 (1956). C.A., 50, 16340 f (1956).
Sublimed, thin films of Agand Tl halides were sensitized by organic dyes. Spectraland photoconductive properties were determined for 42 dyes.

23. "The photoreaction of reversible fading of dyes adsorbed on microporous glass"

V. Karyakin, Zhur. Fiz. Khim., 30, 986 (1956). C.A., 50, 16410h (1956).
The light induced fading of dyes adsorbed on SiO_2 was found to be due to H_2O acting as a reducing agent. Decolorized dyes were regenerated with O_2.

24. "Oxidation enzymes from molds and yeasts. I. The glycolicde-hydrogenase of molds".

W. Franke and I. Schulz, Hoppe-Seyler's Z. physiol. Chem., 303, 30 (1956). C.A., 50, 16891a (1956).
The title mold enzyme reduces acceptor dyes.

25. "The zinc oxide-sensitized photoreduction of thionine and methylene blue".

T. S. Glikman and M. E. Podlinyaeva, Ukrain. Khim. Zhur., 22, 478 (1956). C.A., 51, 3296g (1957).
Dilute aq. thionine solutions are photoreduced in the presence of ZnO with $\Phi = 0.02$-3. The reducing agent is postulated to be $OH^{\ominus}$.

26. "Acceleration of the rate of respiration of sensitized neurons by light".

N. Chalazonitis and A. Arvanitaki, Congr. intern. biochim., Résumés comuns., 3e Congr. Brussels, 1955, 82. C.A., 51, 9020f (1957).
Thionine photosensitizes the neurons of the optic lobe of Sepia to give an increase in the rate of respiratory intensity.

27. "A model for photoöxidation and reduction".

N. Takeyama, Kagaku (Tokyo), 27, 90 (1957). C.A., 51, 9332f (1957).
A molecular model is proposed for the photoreduction of thionine to its leuco form by Fe^{+2}.

28. "Photolithographic material and process"

W. Neugebauer, M. Tomanek and T. Scherer, U. S. Patent 2,768,077, Oct. 23, 1956. C.A., 51, 9388i (1957).
Thionine is used as a polymerization inhibitor to increase the shelf-life of the photosensitive unsaturated ketones used in the process.

29. "Temperature dependence of the electrical conductivity of organic semiconductors"

A. T. Vartanyan, Izvest. Akad. Nauk S.S.S.R., Ser. Fiz, 20, 1541 (1956). C.A., 51, 10243a (1957).

The conductivity of 34 dyes were investigated in vacuum since O_2, NO_2 and H_2S influence electrical properties.

30. "The preparation of stable free radicals in solution by means of ionizing radiation".

A. J. Swallow, J. Chem. Soc., 1957, 1953. C.A., 51, 15281b (1957).
Gamma irradiation of thionine in an ethanol-H_2SO_4 solution produced a stable free radical.

31. "The effects of ultraviolet radiation on aqueous solutions of ferrous salts".

V. D. Orekhov, A. I. Chernova and M. A. Proskurnin, Zhur. Fiz. Khim., 31, 673 (1957). C.A., 52, 98a (1958).
The formation of a ferrous-oxygen complex is postulated.

32. "Lakes formed by the reaction of ammonium molybdate with thionine".

R. Jensen, J. Marquevielle and F. Tayeau, Bull. soc. chim. France, 1957, 1142. C.A., 52, 2130e (1958).
Colored complexes between thionine and ammonium molybdate were prepared. Several different molar ratios were observed.

33. "Influence of concentration on the absorption spectrum and action spectrum of fluorescence of dye solutions".

J. Lavorel, J. Phys. Chem., 61, 1600 (1957). C.A., 52, 4318f (1958).
The long wave length change in the fluorescence spectrum of thionine was concentration dependent and attributed to the formation of a non-fluorescent dimer.

34. "The photogalvanic effect in the thionine-thiosinamine system".

W. Hendrich, Roczniki Chem., 31, 937 (1957). C.A., 52, 5987e (1958).
The effect of pH and added inorganic ions on the potential of the title system is discussed.

35. "The catalytic properties of adsorbed dyes".

V. V. Yushina, Zhur. Fiz. Khim., 31, 2357 (1957). C.A., 52, 8417i (1958).
Thionine was found to be catalytically active toward oxidation of pyrogallol and metol on various substrates.

36. "Photochemical reduction of thionine. I. The thionine-ferrous ion complex".

R. Havemann and H. Pietsch, Z. physik. Chem., 208, 98 (1958). C.A., 52, 9785b (1958).
Thionine (Th) is found to form an isolatable dimer complex ion with ferrous ions ($2ThFeCl_2 \cdot 2HCl$). The photochemical bleaching of thionine by Fe^{++} is explained.

37. "Photochemical reduction of thionine. II. Reversible photochemical reaction of thionine and methylene blue by Fe^{++} in aqueous acetone solution".

R. Havemann and H. Pietsch, *Z. physik. Chem.*, **208**, 210 (1958). *C.A.*, **52**, 13440g (1958).
The effects of various organic solvents on the rate of ferrous-thionine bleaching are discussed in terms of complex dissociation (see ref. 36).

38. "Photoreduction of methylene blue and thionine by ferrous sulfate using flash irradiation".

C. A. Parker, *Nature*, **182**, 245 (1958). *C.A.*, **52**, 19508f (1958).
An investigation to determine whether the intermediate semiquinone radical was formed *via* a triplet or highly excited singlet was conducted.

39. "Wave length effect in flash photolysis".

C. A. Parker, K. Bridge and G. Porter, *Nature*, **182**, 130 (1958). *C.A.*, **53**, 65c (1959).
Reversible photobleaching of thionine in oxygen free H_2SO_4 occurred in the presence of orange-red light. Triplet and semiquinone species were detected.

40. "Relation between the absorption spectrum of oxidation-reduction dyes and pH"

Y. Koyama, M. Masuda and M. Yoshikawa, *Osaka Daigaku Igaku Zasshi*, **10**, 1193 (1958). *C.A.*, **53**, 720f (1959).
The extinction coefficient of a number of redox dyes was influenced by pH but the position of absorption was not.

41. "Determination of ascorbic acid by thionine"

R. Charonnat and L. B-Beauguesne, *Ann. pharm. franc.*, **16**, 96 (1958). *C.A.*, **53**, 1449g (1959).
A colorimetric method is described for the determination of ascorbic acid.

42. "Photopolymerization"

G. Oster, U. S. Patent 2,850,445, Sept. 2, 1958. *C.A.*, **53**, 1844g (1959).
A vinyl compound is photopolymerized in the presence of a dye, oxygen and a mild reducing agent.

43. "Photodegradation mechanism of methylene blue in solution".

Z. Yoshida and K. Kazama, Kogyo Kagaku Zasshi, 60, 190 (1957). C.A., 53, 2822cd(1959).
A semiquinone radical is postulated as the intermediate in the photodegradation of methylene blue. The effect of oxygen is explained.

44. "Kinetic studies of the thionine-iron system"

I. R. Hardwick, J. Am. Chem. Soc., 80, 5667 (1958). C.A., 53, 3900g (1959).
A mechanism is proposed for the photobleaching of thionine in the presence of ferrous ion.

45. "Photochemical reduction of thionine. III. Influence of fluoride on the photochemical system thionine-, selenine 3,7-diamino-phenoxazine- and methylene blue-ferrous ions".

R. Havemann and H. Pietsch, Z. Physik. Chem., 210, 232 (1959). C.A., 53, 13797c (1959).
Thionine is the most rapidly reduced of several dyes studied. The dark reaction is inhibited by fluoride ion.

46. "Reversible phototransformations: the thionine-iron system"

F. Juston-Coumat, Publs. sci. univ. Alger, Ser. B. 4, 47 (1958). C.A., 53, 19534e (1959).
Studies of the red to green change followed by the corresponding e.m.f. are reported for solutions of thionine, $FeSO_4$ and H_2SO_4 in water. The change on illumination is rapid.

47. "The reversible bleaching of thionine by ferrous ions".

J. Schlag, Z. physik. Chem., 20, 53 (1959). C.A., 54, 1041h (1960).
The forward and back reactions were studied with a quick registering spectral photometer.

48. "Utilization of the photosensitized oxidation of sulfite for manometric actinometry".

I. Fridovich and P. Handler, Biochem. et. Biophys. Acta, 35, 546 (1959). C.A., 54, 3578g (1960).
An ultrasensitive actinometric system was designed using the dye activated oxidation of sulfite ion. Thionine was an effective sensitizer.

49. "Energy migration in a system of molecular assemblies".

G. Tomita, et al., Kyushu Daigaku Seisankagaku Kenkyusho Hokaku, 19, 6, 43, 50, 57 (1956). C.A., 54, 1046e (1960).
A series of papers are given concerning dye photoactivated reactions and reaction mechanisms.

50. "Photochemical reduction of thionine. IV. Kinetics of the dark reaction with ferrous ions during the photochemical reduction of thionine. V. Detection of the thionine-ferrous ion complex by kinetic methods".

R. Havemann and K. G. Reimer, *Z. physik. Chem.*, *211*, 26, 63 (1959). *C.A.*, *54*, 52181 (1960).
The dark reaction (oxidation of leucothionine by ferric ion) is first order in leucodye. Kinetic data suggest complex formation.

51. "Preparation and application of thiazine dyes".

V. Vesely and D. Tersijska, *Chem. prumysl.* *5*, 388 (1955). *C.A.*, *54*, 61291 (1960).
Thionine and Toluidine O were prepared by a new method.

52. "Photoreduction of dyes in rigid media. II. Photo-oxidation-reduction properties of thiazine dyes".

B. Broyde and G. Oster, *J. Am. Chem. Soc.*, *81*, 5099 (1959).
The redox properties of 5 thiazine dyes were determined in high viscosity glucose glasses. Viscosity effects were studied. *C.A.*, *54* 6267d (1960).

53. "Water-insoluble, high-molecular weight compounds".

B. Sansoni, Ger. Patent 1,005,734, March 4, 1957. *C.A.*, *54*, 6499 (1960).
Ion exchangers are prepared by reacting aminodyes (thionine) with diazopolyaminostyrene.

54. "Photolysis of thionine in rigid medium".

C. A. Parker and W. T. Rees, *J. chim. phys.*, *56*, 761 (1959). *C.A.*, *54*, 7297g (1960).
When thionine is irradiated at 77°K with u.v. light, a new product is obtained which is probably the semithionine radical. Upon melting, thionine and leucothionine result.

55. "Photochemical reduction of thionine. VI. The photochemical thionine-hydroquinone system. VII. Thionine-ascorbic acid system".

R. Havemann and H. Pietsch, *Z. physik. Chem.*, *211*, 257 (1959). *C.A.*, *54*, 8237a (1960).
Hydroquinone forms a light-sensitive quinhydrone type complex with thionine. A very photosensitive complex is formed between thionine and ascorbic acid.

56. "Absorption spectra for layers of a dye in a vacuum".

L. A. Lyzina and A. T. Vartanyan, *Optika i Spektroskopiya*, *7*, 172 (1959). *C.A.*, *54*, 9492c (1960).
A technique is described for the preparation of thin dye films by sublimation.

57. "Some spectrum peculiarities of thionine violet crystals and solutions".

N. M. Melankholin and E. N. Slavnova, *Optika i Spektrosiopiya*, *7*, 659 (1959). *C.A.*, *54*, 10507h (1960).
Thionine crystallizes from aq. solutions in 2 forms. Its spectrum in conc. solution is different from other thiazine dyes due to unusual hydrogen bonding.

58. "The kinetics of the thionine-ferrous ion reaction".

A. Ainsworth, *Z. Elektrochem.*, *64*, 93 (1960). *C.A.*, *54*, 11662h (1960).
Two mechanisms are proposed for the bleaching reaction.

59. "Photochemical reduction of thionine. VIII. pH dependence of the photochemical reduction of thionine by iron (II) ions"

R. Havemann and K. Reimer, *Z. physik. Chem.*, *213*, 343 (1960). *C.A.*, *54*, 12740a (1960).
The large pH dependence of the photochemical reduction of thionine is due to the effect of pH on the dark reaction. The photoreduction is pH independent but increasing acid concentration speeds up the dark, oxidation reaction.

60. "Electron transfer and absorption spectra of complexes".

S. Ainsworth and E. Rabinowitch, *Science*, *131*, 303 (1960). *C.A.*, *54*, 12774d (1960).
A complex appears to be formed between thionine and ferrous ion. Reduction takes place within 10^{-5} sec. after light absorption.

61. "Efficiency of some Fe-thionine photogalvanic cells".

A. E. Potter and L. H. Thaller, *Solar Energy*, *3*, 1 (1959). *C.A.*, *54*, 15019f (1960).
A very low efficiency cell was constructed (10^{-4} %).

62. "In vitro lens studies. III. Lens potentials".

M. A. Constant, *Am. J. Ophthalmol.*, *47*, 410 (1959). *C.A.*, *54*, 16489e (1960).
Cationic dyes increased the negativity of the lens potential by 0.12 volts. Methylene blue was active.

63. "Photoreduction of porphyrins and the oxidation of amines by photoexcited dyes".

D. Mauzerall, J. Am. Chem. Soc., 82, 1832 (1960). C.A., 54, 21125a (1960).
Certain porphins, but not their metal chelates, undergo photoreduction in the presence of amines. Thionine also undergoes photobleaching.

64. "Sign of photocurrent carrier and relaxation of photoconductivity in thallium and silver iodides sensitized with organic dyes".

I. A. Akimov and E. K. Putseiko, Fotoelek. i Opticheck. Yavleniya v Poluprovod. Trudy Pervogo Vsesoyuz. Soveshchaniya, Kiev, 1957, 301. C.A., 54, 22035g (1960).
A solid-state physical explanation of sensitization in terms of energy transfer is advanced.

65. "Kinetics of the thionine-ferrous ion reaction"

S. Ainsworth, J. Phys. Chem., 64, 715 (1960). C.A., 54, 23639g (1960).
Two concentration dependent reaction mechanisms are proposed.

66. "Chlorophyll-sensitized photoreduction in the thionine-ferrous system".

S. Ichimura and E. Rabinowitch, Science, 131, 1314 (1960).
C.A., 54, 24932d (1960).
The reversible photoreduction of thionine by ferrous can be produced by chlorophyll in the colloidal state in red light absorbed only by chlorophyll.

67. "Some possibilities for solar energy utilization by means of the photogalvanic effect"

S. Anderson, Trans. Conf. Use Solar Energy Tuscon, 4, 168 (1955).
C.A., 54, 25083c (1960).
A ferrous-thionine cell was demonstrated in which separation of the photoproducts is achieved by a starch paste containing the reactants and surrounding one of the electrodes.

68. "Spectroscopic study of the reaction of two dyes in solution"

K. L. Arvan, Doklady Akad. Nauk S.S.S.R., 121, 123 (1958).
C.A., 54, 25835e (1960).
Complex formation between thiazine dyes was studied in various solvents. The properties of the dimers are discussed.

69. "The pH dependence of the dark- and photoreduction of thionine by sulfite ion"

H. Pietsch, Z. wiss. Phot., 54, 109 (1960). C.A., 55, 1247h (1961). The influence of pH on the title system is related to the relative reducing strengths of SO_3^{-2} and HSO_3^-.

70. "Chromatographic separation and isolation of metachromic thiazine dyes"

K. B. Taylor, J. Histochem. and Cytochem., 8, 248 (1960). C.A., 55, 5633f (1961). Paper chromatographic methods for the separation of N-alkylthionines are described along with Rf values.

71. "The effect of water vapor on the absorption spectra of sublimed layers of dyes"

L. A. Lyzina and A. T. Vartanyan, Optika i Spektroskopiya, 6, 484 (1959). C.A., 55, 11073d (1961). Vacuum sublimed dye layers are amorphous. Addition of water vapor caused changes in spectra and aggregation and crystallization in thionine.

72. "The photochemical reduction of thionine by means of trivalent vanadium"

R. Havemann, H. Pietsch and E. Sachse, Z. wiss. Phot., 54, 185 (1960). C.A., 55, 14026c (1961). V^{+3} reduced thionine slowly in the dark but at an increased rate on illumination. V^{+4} does not oxidize leucothionine.

73. "Comparison of the thermal activation energies of electrical conduction with absorption and phosphorescence spectra in a series of organic compounds"

A. T. Vartanyan and L. D. Rozenshtein, Izvest. Akad. Nauk. S.S.S.R., Ser. Fiz., 25, 428 (1961). C.A., 55, 17251f (1961). A comparison of the thermal absorption energy for electrical conduction in the dark with the absorption wavelength and shortest phosphorescence wavelength was made for 36 compounds including thionines.

74. "Thionine derivatives in the extraction and direct photometric determination of boron"

L. Pasztor and J. D. Bode, Anal. Chim. Acta, 24, 467 (1961). C.A., 55, 19602c (1961).

Thionine and derivatives were used in the spectrophotometric determination of boron as BF_4^- by measuring the λ max for the BF_4^--dye complex in various chlorinated hydrocarbon solvents.

. "Comment on Melankholm's article on absorption spectra of thiazine dyes"

J.Meyer-Arendt, J. Opt. Soc. Am., 51, 583 (1961). C.A. 55, 206151 (1961).
Similar effects have been reported for crystals of hexamethylbenzene.

. "Photochemical reduction of thionine. IX. Quantum yield of the photochemical reduction of thionine by ferrous ions"

R. Havemann and K. G. Reimer, Z. physik. Chem. (Leipzig), 216, 334 (1961). C.A., 55, 21764c (1961).
The photochemical reduction of thionine by Fe^{+2} proceeds in proportion to the amount of absorbed light. The quantum yield for wavelengths of 546 and 579 $m\mu$ increases with increasing Fe^{+2} concentration. In acetone solutions, this increase begins at smaller Fe^{+2} concentrations than in aqueous solutions.

7. "Ascorbometric determination of some thiazines and thiazones"

E. Ruzicka and M. Kotoucek, Z. anal. Chem., 180, 429 (1961). C.A., 55, 231881 (1961).
Thionine and certain derivatives can be titrated poteniometrically with ascorbic acid using Pt-saturated Hg_2Cl_2 electrodes and temperatures of 65-75°C. Certain colored molecules interfere.

8. "Electron spin resonance in solid-state samples of phenothiazine and oxazine dyes"

C. Lagercrantz and M. Yhland, Acta. Chem Scand., 15, 1204 (1961). C.A., 56, 5554e (1962).
Methylene blue, thionine and toluidine blue exhibit EPR absorption in the solid state equal in intensity to those reported for the triphenyl methane dyes. The presence of unpaired electrons in the solid state dyes is not completely understood.

9. "Photoreduction of thionine by ferrous sulfate"

G. G. Hatohard and C. A. Parker, Trans. Faraday Soc., 57, 1093 (1961). C.A., 56, 5562g (1962).
From the kinetics of the photoreduction of thionine by Fe^{++} in 0.1N H_2SO_4, it is proposed that reaction occurs via a metastable state of the dye assumed to be a triplet. Semithionine, initially formed, disproportionates to thionine and leucothionine.

80. "Photochemical change of dyes in amide media"

K. L. Arvan and N. V. Ivanova, Zhur. Fiz. Khim. 35, 1215 (1961). C.A., 56, 7468f (1962).
The spectral shift of methylene blue in polyamide films is attributed to photodemethylation.

81. "Kinetic studies of the thionine-iron system II"

R. Hardwick, J. Phys. Chem., 66, 349 (1962). C.A., 56, 10955e (1962).
Fe^{+3} is assigned a chemical, not a quenching, role as an inhibitor of the photoreduction of thionine by Fe^{+2}.

82. "The superadditivity with hydroquinone of photographic developing agents forming positively-charged semiquinones. I. The p-phenylenediamines."

J. F. Willems and G. F. vanVeelen, Phot. Sci. Eng. 6, 39 (1962). C.A. 56, 11109d (1962).
The degree of superadditivity of mixtures of p-phenylenediamine and derivatives with hydroquinone increases with the stability of the semiquinone of the p-phenylenediamine and is related to its half-wave potential.

83. "Photochemical property of mixtures of glycerophosphates"

C. Piffault et al, Bull. Soc. Pharm. Bordeaux, 100, 97 (1961). C.A., 56, 15070h (1962).
Low concentrations of methylene blue in a 21.15 % aqueous solution of Na, K and Mg glycerophosphates was photoreduced to the leuco base by UV or infrared radiation. The methylene blue could be regenerated by passage of O_2 or air through solution. Using a 12% aqueous solution of the glycerophosphates gave the same results but strong radiation produced thionine by demethylation.

84. "Photochemical reactions in pyridine solutions of thiazine dyes"

K. L. Arvan and D. L. Glebovskii, Zh. Fiz. Khim. 35, 2822 (1961). C.A., 56, 15071i (1962).
Dilute solutions of thiazine dyes in pyridine were photoreduced without the addition of a reducing agent. Facts support a complex formation for decoloration.

85. "Photochemical reactions of thiobenzophenones"

G. Oster, L. Citarel and M. Goodmann, J. Am. Chem. Soc., 84, 703 (1962). C.A., 57, 321a (1962).
The photochemical reactions of thiobenzophenone were compared with those of benzophenone.

86. "Electron-spin resonance (E.P.R.) observations on the reduction of methylene blue and related compounds"

P. B. Ayscough and C. Thomson, J. Chem. Soc, 2055 (1962). C.A., 57, 3002b (1962).
Species obtained by X-irradiation of the title compounds are the same as the species obtained by chemical reduction.

87. "Photoreduction of thionine and methylene blue by nitrilotriacetic acid and ethylenediaminetetracetic acid"

J. Joussot-Dubien and J. Faure, Compt. Rend., 254, 3090 (1962). C.A., 57, 4220c (1962).
Tertiary amines, such as aminopolycarboxylic acid complexes, photoreduce aqueous solutions of methylene blue.

88. "Fluorescence excitation spectra and fluorescence sensitivity"

C. A. Parker, Photoelec. Spectrometry Group Bull. No. 13, (1961). C.A., 57, 6753i (1962).
The fluorescence sensitivity of a number of dyes including thionine was calculated from fluorescence excitation spectra.

89. "Dimerization of thionine and some thionine-like dyes"

R. Havemann, E. Nutsch and H. Pietsch, Z. Physik. Chem., 219, 171 (1962). C.A., 57, 12668g (1962).
Dimerization of thionine and similar dyes was examined by optical measurements.

C. FREE RADICAL SENSITIZERS

1. "Styryl dye base composition and photographic processes for producing lithographic surface resists and prints therewith"

R. H. Sprague, H. L. Fichter and W. P. Hamilton, U.S. Patent 3,095,303, filed July 12, 1960. Official Gazette, U.S. Patent Office, June 25, 1963.
A photosensitive composition consisting of an organohalogan compound capable of forming free radicals and a vinylene styryl dye can be made to produce a litho master.