

there was no hope for us. To-day when we are operating at what we consider normal capacity for the looms and dye houses in this country, there are required not less than 150,000 tons of logwood and 50,000 tons of quercitron bark to produce the dyes that are being used for the dyeing of black, blue and yellow, and in proportion to the number of looms engaged in 1918 and those engaged on similar production in 1914, there is actually a little less proportionate use of dyewood extracts than there was in 1914, owing to the difficulty of securing supplies from foreign ports due to the shipping situation, and this has compelled some of the dyers to cut down the quantity of logwood and quercitron extract that they are using and substitute some of the artificial colors instead.

Just one thing more. In the various medical journals there have been some statements appearing recently covering the use of Flavine in gunshot wounds. This has appeared in *Chemical Abstracts*, *American Medicine*, and *The Lancet*, and inasmuch as my company is the only manufacturer of Flavine, which is a trade-marked, registered name for the concentrated yellow dye-stuff made by us from the inner bark of the black oak, I have done all in my power to bring to the attention of those interested that Flavine has no therapeutic action whatsoever. The material wrongfully called Flavine is one of the acridine derivatives used for dyeing yellow, made, I believe, by the Bayer Company, and with their usual disregard for any hampering conventions, they have seen fit to take the name of the best yellow dyestuff they know, namely Flavine, and label their infernal acridine derivative with it. I take this opportunity of drawing attention to this newer use of a natural dyestuff, namely, the labeling of an artificial color with a name that does not belong to it.

PHOTOGRAPHIC SENSITIZING DYES: THEIR SYNTHESIS AND ABSORPTION SPECTRA

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The light sensitiveness of the silver bromide emulsion is at a maximum at the extreme violet end of the visible spectrum, and falls practically to zero in the green. The emulsion, however, may be rendered sensitive to the longer wave lengths by the use of dyes which stain silver halide. Plates with such emulsions are known as panchromatic or orthochromatic plates.

For this purpose certain of the azo dyes, of the rosanilines, and of the phthaleins have been used, but all of these, with the exception of erythrosine, have been superseded by dyes derived from alkylated quinolines.

TYPES OF DYES USED

The quinolinium dyes used for photosensitization fall into four main groups differing in methods of synthesis, in absorption spectra, and in their sensitizing action.

(a) The isocyanines are formed by the condensation of α -methylated quinolinium alkyl halides (quinaldine derivatives) with themselves or with quinolinium halides. They sensitize chiefly in the green and yellow.

(b) The cyanines are formed by the condensation of γ -methylated quinolinium alkyl halides (lepidine derivatives) with quinolinium alkyl halides. They show marked sensitization in the yellow, orange and red.

(c) The "pinacyanoles" are formed by the condensation with formaldehyde of two molecules of quinolinium alkyl halide, at least one of which must be α -methylated. They, too, sensitize in the yellow, orange and red and have largely displaced the cyanines.

(d) The "dicyanines" are formed from α, γ -dimethylquinolinium alkyl halides. They sensitize in the red and infra-red.

All of these condensations take place in alkaline solution.

SYNTHETIC WORK

I—INTERMEDIATES

BASES—(a) Quinoline and Bz-substituted quinolines are prepared by the Skraup synthesis from aniline (or other primary amine), sulfuric acid, glycerin, and a suitable oxidizing agent, preferably arsenic oxide.

(b) Quinaldine and Bz-substituted quinaldines were synthesized by condensing paraldehyde with the hydrochloride of aniline (or other primary amine), with or without an oxidizing agent.

(c) Lepidine was formed by reduction (by dry distillation with zinc dust) of lepidone, which had been made by condensing aniline with acetoacetic ester.

(d) α, γ -dimethyl quinoline and Bz-substituted derivatives were synthesized by treating with hydrochloric acid gas, a mixture of acetone and paraldehyde, and then condensing with the hydrochloride of aniline (or other primary amine).

In general, the yields are unsatisfactory.

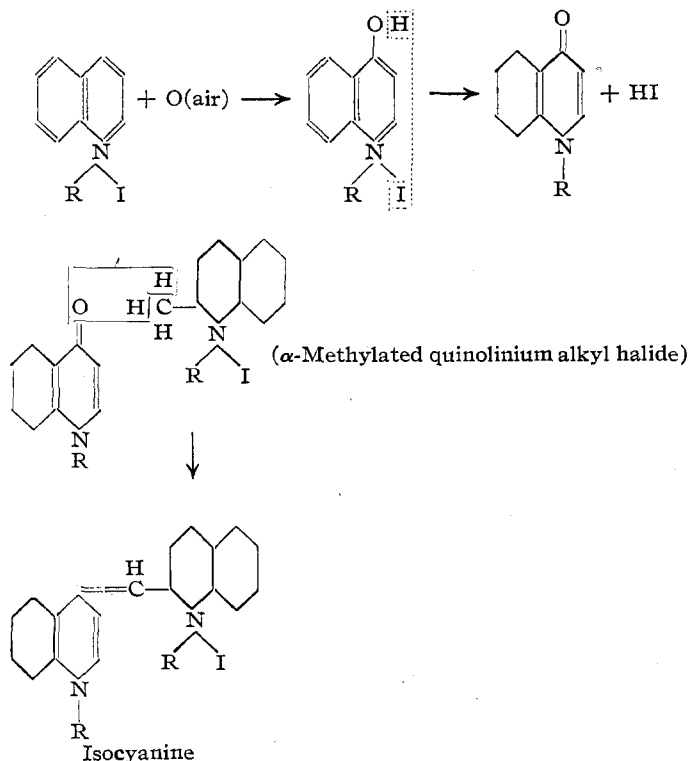
QUATERNARY HALIDES—The quaternary iodides were formed by the addition of methyl (or ethyl) iodide to the base, with or without a solvent. In general, the best yields were obtained without solvent and with the reagents in equimolecular proportions.

These substances are crystalline solids of a more or less pronounced yellow color. They are readily purified by crystallization from alcohol, and their iodine content is easily determined since they yield all their iodine as iodide ion in aqueous solution.

The quaternary iodides may be quantitatively converted into the corresponding chloride or bromide by treating their aqueous solutions with freshly precipitated silver chloride or bromide.

II—DYES

(a) The method of synthesis has already been given. In the case of the isocyanines the course of the reaction is probably as indicated:



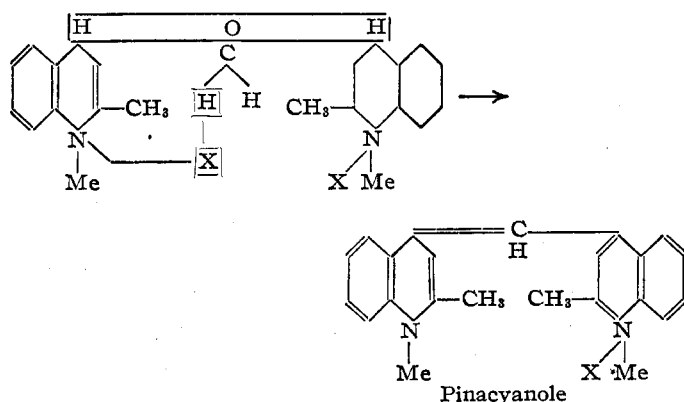
The pairs of intermediates used in the preparation of our isocyanines are listed in Table I as Nos. 1, 2, 3, 4, 5.

TABLE I

No.	PAIR	W.L.	Ext.	W.L.	Ext.	Ratio
<i>Isocyanines</i>						
1	Quinaldine MeI + Quinoline MeI.....	558	51
2	Toluquinaldine MeI + Toluquinoline MeI.....	562	171
3	Toluquinaldine MeI + Quinoline MeI.....	558	180
4	Toluquinaldine MeI + Quinoline EtI.....	560	182
5	Quinaldine MeI + Toluquinoline MeI.....	558	186
<i>Pinacyanoles</i>						
6	Quinaldine MeI.....	605	198	563	111	0.56
7	Toluquinaldine MeI.....	611	290	568	135	0.55
8	Quinaldine MeI + Quinoline MeI.....	605	330	562	152	0.46
9	Quinaldine MeI + Toluquinoline MeI.....	606	218	562	102	0.47
10	Toluquinaldine MeI + Quinoline MeI.....	611	374	568	162	0.43
11	Toluquinaldine MeI + Toluquinoline MeI.....	611	288	568	138	0.48
12	Quinaldine EtI + Quinoline EtI.....	Not examined				
<i>Dicyanines</i>						
13	2,4-Dimethyl Quinoline MeI.....	653	175	606	92	0.53
14	2,4-Dimethyl Quinoline EtI.....	656	44	607	36	0.82
15	2,4,6-Trimethyl Quinoline MeI.....	Not examined				

(b) We have prepared only very small quantities of the cyanines. The mechanism of the reaction is undoubtedly similar to that of the isocyanines.

(c) The course of the reaction to form the pinacyanoles has not been established but is very probably



We have used the pairs of intermediates numbered 6, 7, 8, 9, 10, 11 and 12 in Table I in the preparation of pinacyanoles.

(d) The reaction for the formation of the dicyanines is decidedly obscure.

We have made dicyanines from the intermediates numbered 13, 14 and 15 in Table I. All these products have proved to be decidedly impure.

Determination of the iodine content of dyes of the isocyanine and pinacyanole types has indicated in both cases that the nitrogen-iodine ratio is 2 : 1.

ABSORPTION SPECTRA

The spectrophotometric measurements were made with a König, Martens, and Grünbaum spectrophotometer. The dyes were studied in 95 per cent alcohol solution, in a cell 1 cm. thick against a similar cell containing solvent alone. The concentrations of solutions used were 0.02 g. per liter, 0.01 g. per liter, or 0.005 g. per liter, according to the maximum absorbing power of the substance.

The results are given in Table I in terms of the specific extinction coefficient of the dye, that is, the number of liters of solution in which 1 g. of the dye should be dissolved to give a solution, a 1 cm. layer of which would reduce exactly tenfold the intensity of a beam of light of the wave length in question.

Table I gives the intensity and location of the absorption maxima for a number of dyes synthesized. The dyes of the same type show very similar spectra, as can be seen from the table.

THE COLOR LABORATORY OF THE BUREAU OF CHEMISTRY

A BRIEF STATEMENT OF ITS OBJECTS AND PROBLEMS

By H. D. GIBBS, Chemist in Charge, Color Laboratory,
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It is not my intention this morning to report on any finished work, but merely to give you a sort of airplane view of some of the problems that we have in hand.

About two years ago it was decided to organize the color work of the Bureau of Chemistry. This work originated with the investigation of the dyes employed for coloring food products, and had been carried on in various laboratories of the Bureau for about ten years. It included the identification, analysis, and physiological investigations, and the entire object was the solution of problems arising from and necessitated by the enforcement of the Food and Drugs Act.

The organization of the work to take up problems dealing with the manufacture and utilization of colors is a logical step and a natural extension of the usefulness of the organization. The plan provided for laboratory investigation of colors, both natural and artificial, and the substances entering into their composition, by chemical and physical methods, and the reproduction of laboratory processes on a technical scale. The study of the behavior of substances in large masses necessitated the installation of manufacturing appliances. To accomplish this a rather unique building is in course of erection and equipment on the property of the Department of Agriculture on the Potomac River directly opposite Washington.

This building is 150 ft. by 70 ft., and contains nine chemical and physical laboratories, a library, machine shop, boiler room, engine room, a technical floor 150 ft. by 40 ft., storage rooms, locker rooms and showers.

The equipment will include two 100-h. p. boilers, a 10-ton overhead crane, a 5-ton ice machine, storage battery equipment, all varieties of electric current from a power line of 6,600 volts down, nitrators, sulfonators, fusion kettles, evaporators, autoclaves, dryers, stills, centrifugal machines, and many other large pieces of apparatus in addition to a complete laboratory equipment of chemical and physical apparatus. A railroad siding terminates in the building. Each apparatus is equipped with its own electric motor, where necessary to make a complete unit permitting moving to any desired position as a whole, just as we move the apparatus on a laboratory table. The larger part of the apparatus will be removed from the technical floor when not in actual operation.

The entire equipment is not ready as yet, for the reason that the building is only about one-half completed and war emergency work occupies the completed portion. Adjacent to the main building is a smaller structure for use in our studies on chlorination and other noxious gases that might damage machinery in the larger building.

LABORATORY STUDIES

The laboratory studies naturally have predominated over the plant studies to the present time, for the reason that the laboratory studies naturally come first, and that our own plant has not been completely available for the large scale investigations, except in the case of the chlorination reactions. However, several large-scale operations have been attempted.

The laboratory studies have been progressing along a variety of lines ever since the establishment of the organization. The aim has been to study the development of processes that would be able to withstand competition, and this goal is best reached by the study of conditions underlying yields and costs. We have not been interested in "war babies" that were not directly concerned with the winning of the war. Many problems of the latter nature have been taken up, and if any apology is to be