boiling for five minutes may result in appreciable losses. However, longer incipient boiling, beyond that necessary to reduce the peroxygen, has no effect on the consistency of the results. This has been verified experimentally.

This method has been used to analyze various peroxygen compounds, such as water insoluble acyl peroxides in the pure state, in solution and in solid mixtures; peroxygen in aldehydes, ketones, ethers, vegetable and mineral oils, and sterols; and hydrogen peroxide and related peroxygen compounds.

Among several other solvents that have been tried, ethanol (preferably absolute) has also been found suitable.[5] Absolute methanol is unsuitable as it reacts with the reagents. Although acetone is an excellent mutual solvent, produces no blank, and the reaction is rapid even at room temperature, low and inconsistent results are obtained with acyl peroxides.

A comparison of results using the various solvents is given in Table I. Recrystallized benzoyl peroxide was used as a source of peroxygen. In each case 0.1000 g. was added to 25 cc. of solvent (isopropanol, ethanol or acetone) containing 1 cc. of saturated potassium iodide and 1 cc. of glacial acetic acid. The hot solutions were titrated with 0.1 *N* thiosulfate after holding at incipient boiling for two minutes. For glacial acetic acid the method of Liebhafsky and Sharkey, employing sodium bicarbonate to eliminate the "oxygen error," was used.[1c] All results are given in duplicate.

TABLE I

Solvent	% Purity as benzoyl peroxide	
99% Isopropanol	98.4	98.6
95% Ethanol	98.4	98.5
Acetone	67.8	70.5
Acetic Acid[a]	96.5	97.0

[a] The solutions were prepared according to Liebhafsky and Sharkey and immediately boiled for two minutes and titrated while hot.

With the alcohols and with the acetic acid, no further liberation of iodine occurred on reheating.

Summary

A simple iodometric method for determining peroxygen in organic compounds, involving the use of isopropanol as the solvent medium, is described. No blank is required with this solvent. The method is flexible and readily adaptable to various types of peroxygen compounds.

NEW YORK, N. Y. RECEIVED DECEMBER 23, 1940

Particle Size in the Vat Dyeing of Cellulose[1]

BY E. I. VALKO[2]

In vat dyeing, the dye passes through an oxidation–reduction cycle. The original insoluble dye compound (consisting mostly of a quinone) is first converted, by an aqueous reducing solution, into the soluble leuco form (consisting mostly of the alkali salt of a hydroquinone), in which form it is adsorbed by the fiber. The adsorbed leuco compound is then oxidized back to the original compound by air or an aqueous oxidizing solution. The dyeing operation is terminated by an aftertreatment with a hot aqueous soap solution. The three phases of dyeing, reduction, oxidation and aftertreatment, are accompanied by changes of the size of the dye particles. These changes are the subject of the present investigation.

Particle Size of Commercial Vat Dyes.—The tendency of the producers is to make their dyes with the smallest possible particle size in order to secure rapid solution and good yarn penetration, especially when the dye is applied in a printing paste. The dimensions attained are generally below the resolving power of ordinary microscopes. Although gravitational settling is hopelessly slow, a suitable centrifuge gives conveniently measurable rates of sedimentation velocity. In coöperation with Dr. Walter Wolff, an instrument was built, based on the design of Svedberg,[3] which allows the photographic recording of the settling to be carried out during centrifuging. As a much less intense centrifugal field is sufficient, many of the attachments and refinements of Svedberg could be omitted. The results on Indanthrene Brilliant Red FFB powder may be mentioned as an example. Photographs of the suspension were taken at 2000 r. p. m. at intervals of five minutes during one hour. The particle size distribution diagram (weight frequency), calculated on the basis of photometric evaluation

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(5) Although ethanol is the commonest organic solvent, for some reason it has been neglected for this determination in the past.

(1) Original manuscript submitted to the Division of Cellulose Chemistry of the American Chemical Society in July, 1938. Presented at the 97th Meeting of the American Chemical Society, April 3 to 7, 1939, in Baltimore, Md.

(2) Present Address: Onyx Oil and Chemical Co., Jersey City, N. J.

(3) Svedberg, *Ind. Eng. Chem., Anal. Ed.*, **10**, 113 (1938).

TABLE I

PARTICLE SIZE OF VAT DYES AS LEUCO SALTS AT 25°

Trade name	Chemical nature of dye	Diffusion coefficient sq. cm./day	Particle radius 10^{-8} cm.	Mol. wt. of the particles exp.	Aggregation no.
Caledon Jade Green	12,12′-Dimethoxy-dibenzanthrone	0.272 ± 0.020	7.89	1874	3.6
Indanthrene Red RK	Anthraquinone-1,2,2′,1′-naphthacridone	.292 ± .001	7.19	1416	3.8
Indanthrene Golden Yellow GK	3,4,8,9-Dibenzpyrene-5,10-quinone	.327 ± .007	6.42	1009	3.3
RK	Dibromo-3,4,8,9-dibenzpyrene-5,10-quinone	.333 ± .004	6.31	963	2.1
Indanthrene Yellow GK	1,5-Dibenzoylaminoanthraquinone	.294 ± .010	7.14	1388	3.1

of the photographs exhibits a maximum at the particle radius of 1.2×10^{-5} cm. About 80% by weight of the dye has a radius between $1–1.5 \times 10^{-5}$ cm. This size is in the upper range of the colloidal field. Each particle contains several million dye molecules.

Similar results were obtained with the other vat dyes investigated.

Particle Size of Leuco Salts.—The diffusion rate is the most suitable measure for the particle size of a dyestuff in solution. It has frequently been used in the study of acid and direct dyes,[4] but with vat dyes the only available data are those of Schaeffer,[5] and these are merely semi-quantitative and not sufficiently detailed. The porous plate method was used in the present investigation. A description of the experimental procedure already has been given elsewhere.[6] The dyes were applied from a solution containing 0.05 g. of sodium hydrosulfite, 0.1 mole of sodium hydroxide and 0.2 mole of sodium chloride per liter. These concentrations were approximately those used in technical dyeing. To eliminate the effect of the electrical diffusion potential, the electrolyte concentration was maintained equal in the inner and the outer cells. The initial dye concentration was 0.1 g. per liter. During the experiments the solution was kept under hydrogen. The vat solutions were analyzed colorimetrically.

Table I shows the results of the measurements.

The particle radius is calculated, assuming a spherical form, from the Stokes–Sutherland–Einstein formula

$$D = RT/6\pi\eta rN$$

where D is the diffusion coefficient, R the gas constant, T the absolute temperature, η the viscosity, r the radius and N Avogadro's number. The weight of the particle is obtained on the basis of an assumed average density of 1.5. The aggregation number represents the average number of dyestuff anions contained in each particle.

The results indicate that on the average three dyestuff ions build one particle or ionic micelle. Considering the kinetic nature of the aggregation equilibrium, it is reasonable to assume that single dye ions are present in a sufficient amount to penetrate the submicroscopic water-filled pores of the swollen cellulose fiber (average pore diameter $4–6 \times 10^{-7}$ cm.)[6] and to be adsorbed by the inner walls of the pores.

Particle Size of Indigosols.—The indigosols are the salts of the acid sulfuric esters of the reduced vat dyestuffs (the hydroquinones) and are adsorbed in this form by the fibers. The same experimental procedure as above was applied. However, only a very low concentration of hydrosulfite and sodium hydroxide was used. Their presence proved necessary in order to maintain stability of the dye during the experiment.

The data for Indigosol Golden Yellow JGK (3,4,8,9-dibenzpyrene-5,10-quinone) and Indigosol Blue JBC (3,3-dichloroindanthrene) were as follows: diffusion coefficient sq. cm./day, 0.300 ± 0.027 and 0.234 ± 0.010; particle radius 10^{-8} cm., 7.00 and 8.97; molecular weight of the particles exp., 1306 and 2810; aggregation number 2.7 and 3.4.

The average aggregation number of the two indigosols investigated is nearly the same as the average aggregation number of the leuco salts (hydroquinones). Only in the single case of dibenzpyrenequinone was the same dyestuff investigated in both forms, and then the approximate equality of the particle size was established.

The findings for the vat dyes and indigosols confirm Schaeffer's semi-quantitative results on diffusion, as well as Rose's[7] observation that the cold-dyeing vat colors and the indigosols quickly permeate a cellophane membrane, thus indicating

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[4] Valko, "Kolloidchemische Grundlagen der Textilveredlung," Julius Springer, Berlin, 1937.

[5] Schaeffer, *Angew. Chem.*, **46**, 618 (1933).

[6] Valko, *Trans. Faraday Soc.*, **31**, 230 (1935).

[7] Rose, *Ind. Eng. Chem.*, **25**, 1265 (1933).

a low particle size. It should be noted that the vat dyes which were the subject of the present investigation were all of the cold dyeing type. No relation was found between the substantivity and the particle size of the dyes, the former having been found to vary considerably for some of the dyes investigated.[8]

Particle Size and Crystallization of Vat Dyes in the Adsorbed State.—The vat-dyed cellulose fiber, like that dyed with direct colors, reveals under the microscope no inhomogeneity of the dyestuff distribution, provided it is not subjected to an aftertreatment. Haller[9] notes that fibers dyed with certain dyes show microscopically visible dye particles after treatment with boiling water. Different colors vary in their tendency toward aggregation. Haller and Ruperti[10] and later Haller and Okany-Schwarz[11] found that indigo readily forms aggregates when aftertreated with boiling water. With indanthrene dyes, however, only protracted steaming under pressure yielded microscopically-visible particles.

It appeared to be warranted to study the aggregation phenomena with the aid of X-ray diagrams of dyed cellulose material. It was reported by Bion[12] that on the diagrams obtained from ramie fiber dyed with dyestuffs of different types, only the pattern of the cellulose itself was recognizable. However, since the ramie fiber under ordinary conditions takes up only a very small percentage of dyes, it is likely that the amount of the dye on the fiber in Bion's experiment was too small to give a diffraction pattern, even if dye crystals were present.

In the present investigation, it was found that under proper conditions, it is possible to incorporate up to about 60 g. of dye into 100 g. of cellulose material. Following are the amounts of the direct dye Sky Blue FF adsorbed by 100 g. of cellulose at 60° in fifteen days from a bath containing 5 g. of dyestuff and 2 mols of sodium chloride per liter: bleached cotton 9 g., viscose rayon 22 g., cuprammonium rayon 37 g., viscose staple fiber 36 g., Cellophane 44 g., Cuprophane film (cuprammonium process) 46 g. Fifteen days were required to approximately establish the adsorption equilibrium. Obviously there exists a correlation between the amount of dye adsorbed and the extent of the submicroscopical water-filled channels of the swollen cellulose material.

The maximum adsorption of vat dyestuffs by cellulose was found to be of the same order as that of Sky Blue FF reported above, the single values varying widely among the different dyes. These very heavily dyed samples proved suitable for the examination of the question of the physical state of the dye on the fiber, using X-ray diffraction photographs. This part of the investigation was carried out in coöperation with Dr. G. von Susich (Ludwigshafen am Rhein, Germany).

The procedure consisted in comparing the diffraction photograph of the dyed cellulose material with that of the undyed material on the one hand, and with that of the dyestuff itself on the other hand. Copper Kα radiation was used. Sheet cellulose was the most suitable material, not only on account of the high dye content which could be incorporated, but also because the possibility of an external surface deposit of dye could be easily excluded and a sufficiently uniform distribution of the dye readily attained. The dye concentration in the dyeing bath was 5 g./l. and a very high liquor–goods ratio was maintained. In some cases, the dyeing time was extended up to fifteen hours. The aftertreatment consisted in soaking the dyed material for one-half to one hour in boiling water containing 4 g./l. of Castile soap.

To determine the dye content the dyed cellulose material was destroyed at room temperature with concd. sulfuric acid and the solution obtained was matched colorimetrically against solutions of known amounts of dye and cellulose in sulfuric acid.

The experiments lead to the conclusion that a distinction is to be made between three different groups of dyes. The *first group* consists of dyes which are amorphous on the dyed material and remain so upon aftertreatment, *e. g.*, Indanthrene Blue RS (indanthrone). On the diagram of a Cuprophane sheet containing as much as 30% of the dyestuff, the only visible pattern is that of the undyed material, namely, the pattern of mercerized cellulose. The diagram does not change if the material is subjected to the aftertreatment.

It may be added that the behavior of a single direct dye, Sky Blue FF, was investigated and yielded the same result. The Cuprophane film contained 20% dyestuff and the aftertreatment

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(8) Bader, *Bull. Fed. Int. Ass. Chim. Text. Coul.*, Vol. II, p. 169 (1937).

(9) Haller, *Melliand Textilber.*, **6**, 664 (1925).

(10) Haller and Ruperti, *Cellulosechem.*, **6**, 189 (1925).

(11) Haller and Okany-Schwarz, *Helv. Chim. Acta*, **17**, 761 (1934).

(12) Bion, *Helv. Phys. Acta*, **1**, 165 (1928).

was carried out with a concentrated solution of sodium chloride in order to prevent the removal of the dye. It is not unlikely that all direct dyes would exhibit the same behavior.

The *second group* consists of dyes which are amorphous on the fiber after adsorption and oxidation, but form crystallites on aftertreatment. This type of behavior seems to be the most frequent with the vat dyes. Figure 1 shows the result of the X-ray examination of one of the typical representative of the group, Caledon Jade Green. Only the lines due to the pattern of mercerized cellulose can be recognized after the oxidation of the dye. Following the customary aftertreatment, however, the diagram is a superposition of the pattern of the cellulose and of that of the dyestuff. Under the microscope, the dyed material remains completely homogeneous, even upon aftertreatment. The size of the crystallites does not reach the limit of visibility. Estimated on the basis of the width of the diffraction rings, the radius of the crystallites is in the range of the range $5–10 \times 10^{-6}$ cm. It is interesting to note that cotton containing 5.7% Caledon Jade Green failed to exhibit any pattern other than that of native cellulose, while viscose rayon containing 11.9% exhibited the pattern of the dyestuff if subjected to the aftertreatment, although not so clearly as the more heavily charged Cuprophane.

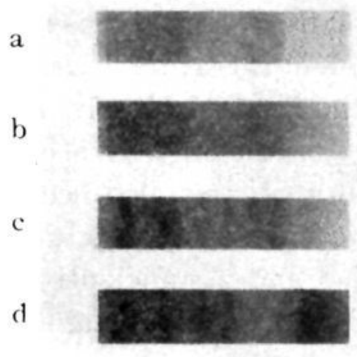

Fig. 1.—X-Ray diagrams: (a) Cuprophan film undyed; (b) Cuprophan film dyed with 29.9% Caledon Jade Green, after oxidation; (c) same, after oxidation and 30 min. treatment with boiling soap solution; (d) Caledon Jade Green.

Bean and Rowe[13] studied microscopically the behavior of Caledon Jade Green on viscose rayon and stated that aggregation to very minute particles occurred only upon steaming for three hours under 50 lb. pressure per sq. in. Our results show that even mild treatment with boiling water produces an aggregation to crystalline particles, which are, however, microscopically invisible.

Another member of the group is Indanthrene Brilliant Scarlet RK. The shade of the cellulose dyed with this dye is strongly shifted from yellow to red by aftertreatment. The X-ray diagram reveals that the color change is due to the crystallization of the dye (Fig. 2). Even soaking in cold water for several hours is sufficient to effect the crystallization. With this dyestuff, the crystalline particles are microscopically visible. Soaping of rayon dyed with this dye adversely affects its luster.

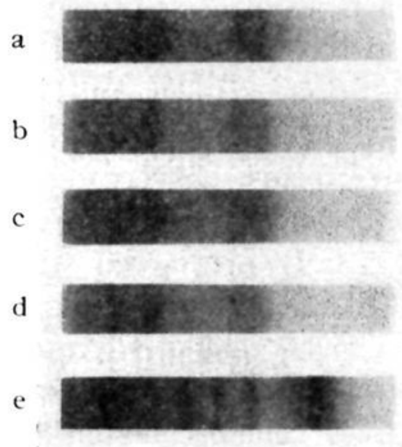

Fig. 2.—X-Ray diagrams: (a) Cuprophan film undyed; (b) Cuprophan film dyed with 14.4% Indanthrene Brilliant Scarlet RK, after oxidation; (c) same, after oxidation and twenty-four hours of soaking in water at room temperature; (d) same, after oxidation and one-hour treatment with boiling soap solution; (e) Indanthrene Brilliant Scarlet RK.

The group also includes Caledon Jade Green 3BS, Indanthrene Blue BC, Indanthrene Golden Orange G, and Caledon Ming Blue XS, but their tendency toward crystallization varies somewhat.

Finally, the *third group* consists of dyestuffs which crystallize upon oxidation, without being subjected to any aftertreatment. Only indigo could be identified by us as a member of the group (Fig. 3). Here, treatment with soap brings no change in the diagram. Indigo crystallites have also been microscopically observed on the fiber by Haller,[9] and by Bean and Rowe,[13] though only aftertreatment with boiling water. Simultaneously with our experiments (*vide* also[14]), Astbury and Dawson[15] observed by X-rays the appearance of indigo crystallites on aftertreated wool.

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[13] **Bean and Rowe,** *J. Soc. Dyers Colourists,* **45,** 67 (1929).

[14] **Valko,** *Wollen- und Leinen-industrie,* **58,** 1 (1938).

[15] **Astbury and Dawson,** *J. Soc. Dyers Colourists,* **54,** 6 (1938).

In order to understand the aggregation phenomena of the vat dyestuffs on the fiber, one has to bear in mind that the sorption of the vat dyes and of the indigosols, as well as that of the direct dyes, is due to the molecular attraction between the cellulose molecule and the dye molecule. Under these circumstances, crystallization of the dye previous to oxidation is impossible because the dye-bath is not supersaturated with dye. Through oxidation, however, the vat dye becomes insoluble. Thereafter the monomolecular layer of the dye on the wall of the submicroscopic pores of the cellulose becomes unstable or metastable. Depending upon the adhesion strength and the magnitude of the tendency to crystallize, the monomolecular film will be disrupted more or less easily and form aggregates of submicroscopic or even of microscopically visible crystallites. The formation of crystalline particles in the fiber can proceed only by an enormous widening of the pores, even if the particles remain microscopically invisible.

As technically important aspects of the phenomenon, there may be mentioned changes in shade, in luster, in fastness to light and to rubbing, and in the tendency of the dye to cause deterioration of the fiber.

Summary

The particle size of commercial vat dyestuffs was investigated by photographic recording of the sedimentation during centrifuging. The average particle radius was found to be about 10^{-5} cm.

The particle size of cold-dyeing vat dyes in the leuco state and of indigosols in solution was investigated by means of diffusion measurements. The average aggregation number was found to be 3.

Crystallization phenomena of vat dyes adsorbed on the fiber were studied by means of X-ray diagrams and the dyes classified into three groups according to whether they remain amorphous, crystallize by aftertreatment, or simply by oxidation.

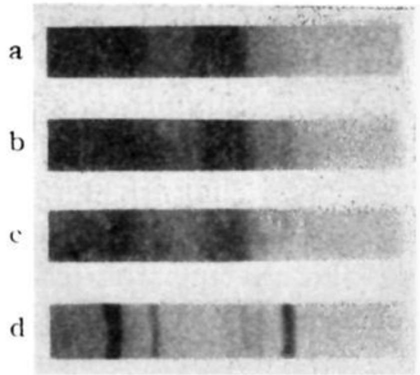

Fig. 3.—X-Ray diagrams: (a) Cuprophan film undyed; (b) Cuprophan film dyed with 9.8% indigo, after oxidation; (c) same, after oxidation and thirty-minute treatment with boiling soap solution; (d) Indigo.

MONTREAL, CANADA RECEIVED JANUARY 24, 1941

[CONTRIBUTION FROM THE DANIEL SIEFF RESEARCH INSTITUTE]

Synthesis of Lipophilic Chemotherapeuticals. III.[1] Remarks on the Properties of Halogen-acylureas, Amides and Related Compounds

BY F. BERGMANN AND L. HASKELBERG

Pearl and Dehn[2] recently reported the physical characteristics of the halogen-acetylureas. We have studied the toxicological and pharmacological properties of chlorinated acetylureas and related compounds, and in view of their general interest we should like to give a brief report of our results.

From Table I it is evident that in the different series of compounds studied, the monochloroacetyl derivatives always show the greatest toxicity while the toxicity of the dichloro compound is less than or equal to that of the trichloroacetyl derivative. No general correlation can be established, therefore, between the halogen content and the poisonous effect; the behavior of the trichloroacroyl derivatives confirms this view.

As the introduction of halogen atoms increases fat-solubility, one should expect in the series of amides a similar "central" effect as in diethyl chloro- and bromo-acetamide[3] and the corresponding diethylamide. The narcotic influence of the chlorine atoms appears to be much less than that of bromine. The dichloroacetamide exhibits a slight narcotic action, the trichloro derivative

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[1] Original manuscript received April 26, 1940. Part I, *J. Chem. Soc.*, 1 (1939); II, *ibid.*, 576 (1940).

[2] Pearl and Dehn, THIS JOURNAL, **61**, 1377 (1939).

[3] *Chem. Zentr.*, **95**, II, 1485 (1924); Fuchs, *Z. angew. Chem.*, **17**, 1505 (1904).