ON THE FADING OF DYESTUFFS. I. PHOTOCHEMICAL DECOMPOSITION OF MALACHITE GREEN AND CRYSTAL VIOLET.

By Kenji IWAMOTO.

Received May 29th, 1935. Published September 28th, 1935.

Although it has long been known that dyed fabrics are decolourised by the action of light, it is only quite recently that this phenomenon has been studied chemically. The phenomenon has been accounted for by several authors as oxidation, reduction, or photochemical reaction, according to the varieties of colouring matter used.

The research on this subject is very difficult, owing to the influence dependent on the following factors: (1) light source, namely intensity and wave-length of acting rays, (2) surrounding atmosphere, (3) temperature, (4) added reagents, and (5) varieties of fibres. The mechanism of fading would be qualitatively inferred from the standpoint of organic chemistry, if the decomposition products could be isolated and their constitutions determined exactly. However, our knowledge on this line is still too meagre to permit of generalisation.

Seyewetz and Mounier(1) found that textiles of animal or vegitable fibres impregnated with nitrophenols or nitroamines turn brown by day-

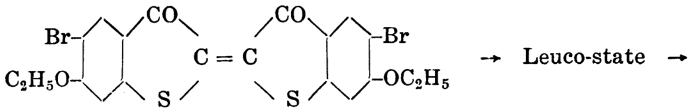
---

(1) *Bull. soc. chim.*, (4), **43** (1928), 648.

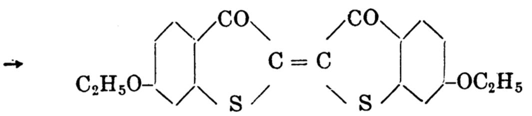
light or ultraviolet rays instead of being decolourised as other dyestuffs, owing to the probable formation of hydroxyazo-compounds.

Hibbert⁽²⁾ exposed pieces of calico dyed with Indigo to sunlight or ultraviolet rays and isolated a yellow powder, m.p. 200°. This substance gave an indophenine reaction and was identified as isatin. Since isatin is also produced by the action of potassium permanganate and sulphuric acid on the same fabric, it appears that the fading of Indigo is due to the formation of isatin by its oxidation. A similar result was again observed by Haller and Ziersch⁽³⁾ separately. Hibbert also obtained phthalic acid from Purpurine (1,2,4-trihydroxy-anthraquinone) and proved that the reaction was due to oxidation.

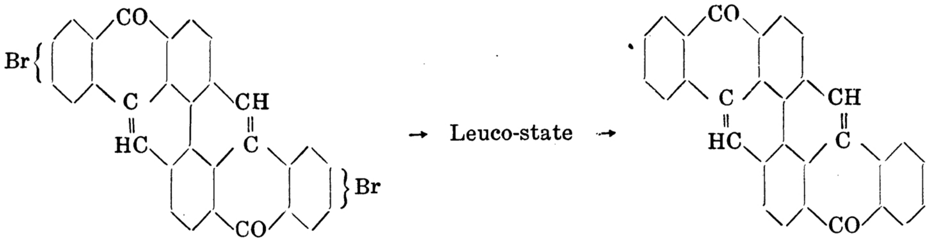
Weber⁽⁴⁾ stated that when viscose rayon was exposed to sunlight in a dye-house, while being dyed with Helindone Fast Scarlet R, orange stripes, due to the formation of Helindone Orange R, appeared. Similarly, Indanthrene Gold Orange 4R, belonging to anthraquinone vat dyes, was changed into Indanthrene Gold Orange G:



Helindone Fast Scarlet R



Helindone Orange R.



Indanthrene Gold Orange 4R Indanthrene Gold Orange G.

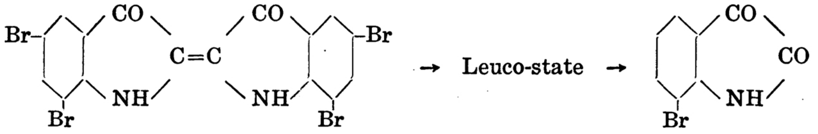
---

(2) *J. Soc. Dyers Colour.*, **43** (1927), 292; *ibid.*, **44** (1928), 377.

(3) *Melliand Textilberichte*, **10** (1929), 951.

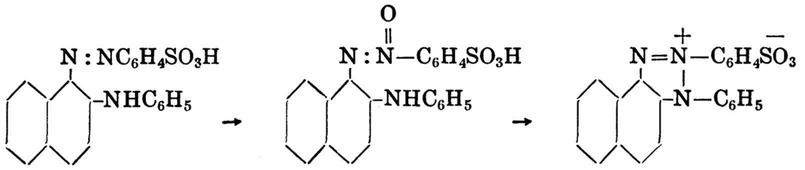
(4) *Rayon Record*, **7** (1933), 227; *Am. Dyestuff Rep.*, **22** (1933), 157.

In other words, if halogen atoms are introduced into the benzene nuclei of vat dyes, the dyes are made very labile in the leuco-state to the light. In some special cases, Brilliant Indigo 4B undergoes not only dehalogenation, but also oxidation, and bromoisatin is formed:



Brilliant Indigo 4B Bromoisatin.

Krollpfeiffer, Mühlhausen and Wolf⁽⁵⁾ studied the action of light on azo-dyestuffs and found that aryl-β-naphthylaminoazobenzene sulphonic acid gives rise to triazonium compound on exposure to light. This change may also be accounted for by the formation of azoxy-compound and subsequent conversion of the latter into triazonium compound. In this case, the oxidation was considered to be the most important:



Phenyl-β-naphthylaminoazobenzene sulphonic acid Azoxy-compound Triazonium compound.

So far as we are aware, no definite compound appears to have been isolated in the decolourisation of triphenylmethane dyestuffs. Therefore, the present author has synthesised some pure dyestuffs and studied their decomposition products. In order to simplify the conditions of experiment, the powdered dyestuffs were spread in a thin layer in a large glass dish, covered with Vita-glass or cellophane paper, and exposed to direct sunlight with occasional stirring. In this manner, Malachite Green (oxalate) was rapidly changed into brown powder. The product was extracted with ether and the ethereal solution was evaporated to dryness. The faint, yellow crystals, melting at 90.5–91°, were identified as *p*-dimethylaminobenzophenone by the mixed melting point method.

Crystal Violet (oxalate) was then exposed to sunlight in the same manner, and the pale yellow crystals thus obtained, m. p. 173–174°, were identified as Michler's ketone by comparison with the pure synthetical substance. On the other hand, Georgievices⁽⁶⁾ isolated the same ketone

---

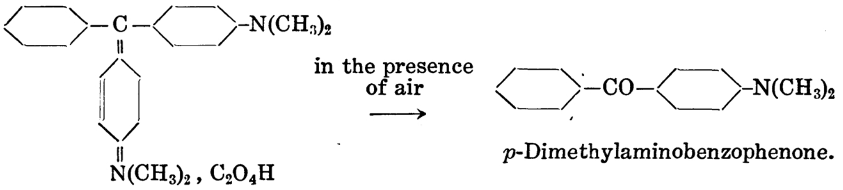
(5) *Ann.*, **508** (1933), 39.
(6) *Ber.*, **38** (1905), 886.

by treating a cold aqueous solution of Crystal Violet with hydrogen peroxide and ammonia. The formation of benzophenone derivatives is interpreted as being caused by either oxidation or hydrolysis.

In order to ascertain whether these reactions are due to oxidation or hydrolysis, the present author exposed the same dyestuffs in a sealed tube to sunlight.

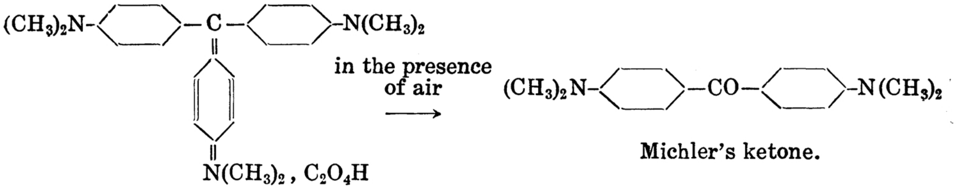
The product obtained from Malachite Green was extracted with ether. Nothing definite could be isolated from the ethereal solution, perhaps owing to the presence of impurity and to the small quantity of the material used. Nevertheless, the properties of the residue from the ethereal solution resembled leuco Malachite Green.

A grey substance from Crystal Violet was extracted with benzene and the colourless crystals, melting at 173–174°, which, on standing in the air, coloured blue gradually, were obtained and proved to be identical with leuco Crystal Violet by means of the mixed melting point method. It thus follows that the reduction occurs in this case, as shown in the following scheme:



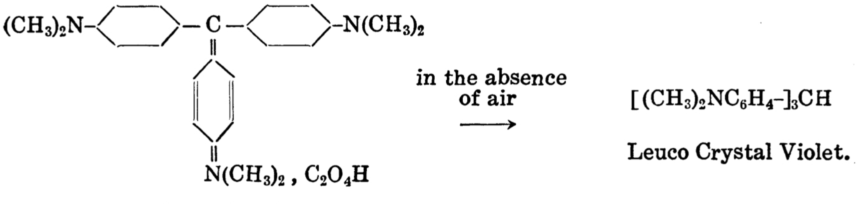
Malachite Green

p-Dimethylaminobenzophenone.



Crystal Violet

Michler's ketone.



$[(CH_3)_2NC_6H_4-]_3CH$

Crystal Violet

Leuco Crystal Violet.

It will be seen from the above facts that oxidation took place actually in the case where photochemical reaction might be expected. Therefore, it may be said that oxidation plays an important part in the fading of dyestuffs of this class.

Further experiment on the same line is now in progress.

Experimental.

Purification of Malachite Green. Commercial Malachite Green (50 g.) was powdered and treated with concentrated ammonia (100 c.c.) in a mortar, when the whole became colourless and the amino-base was deposited. This was collected, washed well with water, and dried. After three crystallisations from ligroin, it separated in colourless crystals which melted at 138°. The amino-base thus purified (10 g.) was dissolved by boiling with a solution of 8 g. of oxalic acid in 100 c.c. of water, when a blue solution was obtained, which was filtered. On cooling the filtrate, the small crystals of Malachite Green oxalate separated out. This was collected and recrystallised from water, when it separated in small scales and was used for next experiment without further purification.

Action of Sunlight on Malachite Green in the Air. The dye thus purified (2 g.) was ground in a mortar, spread in a Petri glass dish in a thin layer, covered with Vita-glass made by Tokyo Electric Company, and exposed to direct sunlight for about two months in autumn, when it was decomposed and changed into a dark brown powder. The product, amounting to 1.7 g., was extracted with ether and the ethereal solution was evaporated. The greenish crystals (0.54 g.) were recrystallised once from ether and then twice from dilute alcohol, from which they separated in faint, yellow crystals and melted at 90.5–91°. The melting point was unaltered by admixture with an authentic specimen of *p*-dimethylaminobenzophenone. Therefore, there can be no doubt that the substance, melting at 90.5–91°, is identical with *p*-dimethylaminobenzophenone.

For the identification of the above-mentioned substance, *p*-dimethylaminobenzophenone $(CH_3)_2NC_6H_4COC_6H_5$ was synthesised by a method described in the description of the German patent No. 41751. To a mixture of benzanilide (10 g.) and dimethylaniline (20 g.), phosphorus oxychloride (10 g.) was added and the whole was heated gradually on a water-bath with vigorous stirring. After the reaction had ceased, the oily product, $C_6H_5C(:NC_6H_5)C_6H_4N(CH_3)_2$, was hydrolysed by heating with hydrochloric acid. After being recrystallised from dilute alcohol, it melted at 90–91°.

Action of Sunlight on Malachite Green in a Sealed Tube. Malachite Green (0.5 g.) was powdered, sealed in a tube of Vita-glass, and exposed to sunlight. After a month's exposure, the contents became pale and the pressure inside the tube increased greatly. The product was extracted with ether and the ethereal solution was evaporated. The residue amounted to 0.11 g. and nothing definite could be isolated from it, but its properties resembled leuco Malachite Green.

Purification of Crystal Violet. Crystal Violet (50 g.) was treated with a 10 per cent. solution of caustic soda (200 c.c.) and the precipitate was collected, washed well with water, and dried. This was recrystallised three times from benzene, when it separated in colourless crystals, m.p. 194°. The pure hydroxy-base was changed into a coloured oxalate by boiling with an oxalic acid solution and it was purified further by recrystallisation from hot water.

Action of Sunlight on Crystal Violet in the Air. The oxalate (2 g.) was spread in a Petri dish, covered with a plate of Vita-glass, and exposed to sunlight for two months. The grey powder thus obtained was extracted with benzene and the benzene solution was evaporated, when blue crystals (1.18 g.) were obtained. They were dissolved in dilute hydrochloric acid and filtered. The filtrate was treated with ammonia. The precipitate thus obtained was collected, washed, and dried. The yield was 0.93 g. It was recrystallised from alcohol, when it separated in yellow crystals melting at 173–174°. No lowering of the melting point was caused by admixture with the synthetic specimen of Michler's ketone, m.p. 173–174°.

Action of Sunlight on Crystal Violet in a Sealed Tube. The coloured oxalate (1 g.) was sealed in a tube of thin Vita-glass and exposed to sunlight for a month. The product was extracted with benzene and, after evaporating off the benzene from the solution, the residue (0.26 g.) was recrystallised three times from alcohol, from which it separated in almost colourless scales melting at 172–173°. For the sake of comparison, leuco Crystal Violet was prepared by the reduction of Crystal Violet and it melted at the same temperature as the decomposition product. The melting point was not depressed when mixed with pure leuco Crystal Violet.

Laboratory of Dye-Chemistry,
Kiriu Higher Technical School.