CERTAIN METALLIC DERIVATIVES OF HYDROXY-ANTHRAQUINONES.[1]

By M. L. Crossley.

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Hydroxy-anthraquinones, such as alizarine, anthrapurpurine and flavopurpurine, form copper, cadmium, nickel and iron salts when boiled in an organic solvent with the corresponding metallic chlorides, anhydrous sodium acetate, and nitrobenzene. These compounds appear to be normal salts in which the metal has replaced hydrogen of the hydroxyl groups. Similar hydroxy-anthraquinone salts of other metals have been prepared by this method but have not yet been thoroughly investigated.

These salts are practically insoluble in cold water, but dissolve readily in methyl and ethyl alcohols as well as in acetone, from which solvents they crystallize fairly well.

Wool, when boiled in a water suspension of the copper, cadmium, cobalt, nickel, chromium and iron alizarates, is dyed a pale shade of the color which alizarine gives on wool previously mordanted with the corresponding metallic salt. The dye is evenly distributed through the fiber and appears to be as firmly held by it as in the case when produced in the mordanted fiber. This, it seems to me, is positive evidence that the color produced by alizarine or similar hydroxy-anthraquinones in mordanted fiber is a property of the corresponding normal salt of the metal whose salt was used to mordant the fiber and that it is evidence of a chemical reaction. This does not mean that the dyeing of the fiber is wholly a chemical phenomenon. Undoubtedly, physical phenomena such as surface tension, diffusion, adhesion, the colloidal state, etc., one or several, contribute to the distribution of the dye in the fiber and to its retention by it. On the one hand, Liechte and Suida, Liebermann, Guggiari[2] have expressed the opinion that the alizarine lakes have the composition of normal salts, while, on the other hand, Biltz, Haller and others,[3] think that lake formation is a phenomenon of a colloidal character. It seems to me that the evidence will not justify the conclusion that the formation of an alizarine lake is wholly a physical or a chemical phenomenon, but rather should be interpreted to mean that it is the result of the combined action of physical and chemical phenomena.

I believe the dye to be *in* the fiber and not simply *on* the fiber. Long boiling and scrubbing of the wool dyed with the sparingly soluble alizarine salts mentioned did not result in removing any more dye than was removed by similar treatment of the wool previously mordanted and then dyed with

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[2] *Ber.*, **45**, 2442 (1912).

[3] *Färber. Ztg.*, **489**, 523 (1912).

alizarine. Whatever salt entered the fiber was held as firmly as when produced in it. The fact that the color was evenly distributed through the fiber is also evidence that it was not simply on the surface.

Experimental Part.

Copper Alizarate.—6 g. of powdered C. P. alizarine, 4 g. of cupric chloride, 5 g. of anhydrous sodium acetate, and 100 cc. of nitrobenzene were boiled for 5 hours in a flask fitted with a reflux condenser. The reaction mass was allowed to cool, after which it was filtered, washed with water and then with ether and finally crystallized from methyl alcohol. The yield was 7 g.

It is a dark red substance which is insoluble in cold water and only very slightly soluble in boiling water. It dissolves readily in ethyl and in methyl alcohols, giving a wine-red solution with the former and a darker red solution with the latter. With acetone it gives a dark red solution and with nitrobenzene a dark brown. It gives a dark purple solution with aniline. It is insoluble in ether, benzene, carbon disulfide, chloroform and petroleum ether. It is decomposed by dilute mineral acids.

Calc. for $C_{14}H_6O_4Cu$: Cu, 21.08. Found: 20.86.

Cadmium Alizarate.—A mixture of 3 g. of alizarine, 2.3 g. of cadmium chloride, 3 g. of anhydrous sodium acetate, and 100 cc. of nitrobenzene was boiled in a flask provided with a reflux condenser for 5 hours. The reaction mass was cooled, filtered, washed with water and with ether and then crystallized from methyl alcohol. The yield was 3 g.

It is a purplish brown product which is practically insoluble in water, ether and benzene. It is soluble in methyl alcohol, ethyl alcohol, and acetone, giving wine-red solutions. Mineral acids decompose it.

Calc. for $C_{14}H_6O_4Cd$: Cd, 32. Found: 32.3.

Nickel Alizarate.—6 g. of alizarine, 3 g. of nickel chloride, 5 g. of anhydrous sodium acetate, and 100 cc. of nitrobenzene were boiled for 5 hours in a flask with a reflux condenser. The reaction product was poured into cold water and filtered. It was then washed with water and ether and crystallized from methyl alcohol The yield was 7 g.

It is a dark purple product which is insoluble in water. It dissolves readily in hot methyl and ethyl alcohol, giving dark red solutions. With acetone it gives a brown solution and with aniline an olive-green. It is but slightly soluble in boiling ether and benzene.

Calc. for $C_{14}H_6O_4Ni$: Ni, 19.77. Found: 19.84.

Iron Alizarate.—6 g. of alizarine, 4 g. of ferric chloride, 5 g. of sodium acetate, and 100 cc. of nitrobenzene were boiled for 5 hours in a flask with a reflux condenser. The product was poured into water, filtered, and washed with ether. It was purified by crystallization from acetone. The yield was 7.6 g.

It is a dark red product, insoluble in water, quite soluble in methyl alcohol, ethyl alcohol, and acetone, giving purple solutions, but slightly soluble in ether and benzene.

Calc. for $C_{14}H_6O_4Fe$: Fe, 19.05. Found: 19.8.

The cobalt and chromium salts of alizarine as well as the copper and nickel salts of anthrapurpurine and flavopurpurine were prepared and, with the exception of the cobalt salt of alizarine, which analyzed for $C_{42}H_{21}O_{12}Co$, appear to be normal salts.

Summary.

Copper, cadmium, nickel and iron salts of alizarine are formed when alizarine is boiled with the respective salts of these metals, anhydrous sodium acetate, and nitrobenzene.

These alizarine salts, though slightly soluble in water, penetrate unmordanted wool fiber and produce colors identical with those produced by alizarine in wool fibers mordanted with the respective metallic salts. These dyes appear to be *in* the fiber and not simply *on* the fiber.

The formation of an insoluble alizarine dye in a mordanted fiber is accomplished by the combined action of physical and chemical phenomena.

BOUND BROOK, N. J.

GENTIAN VIOLET—ITS SELECTIVE BACTERICIDAL ACTION.[1]

BY M. L. CROSSLEY.

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Shortly after the United States entered the war, it was discovered that the supply of gentian violet dye used in biological work as a differentiating stain was limited. Prior to the war, this material had been imported from Germany and no particular attention had been given to its composition. Careful study of the available literature gave no information of importance and it was decided to undertake an investigation of the product in order to determine its composition. Some of the information found in the literature was later discovered to be erroneous or confusing. For example, Pappenhein[2] states that it belongs to the rosaniline group and probably contains dextrine. This fact proved to be correct. On the other hand, Muhr and Richie[3] consider it synonymous with benzyl violet and pyoktanin. This, of course, is an erroneous judgment, for benzyl violet is a mixture of benzyl-pentamethyl-*p*-rosaniline hydrochloride and hexamethyl-*p*-rosaniline hydrochloride, while pyoktanin is a trade name for a mixture of hexamethyl-*p*-rosaniline hydrochloride and pentamethyl-*p*-

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[2] *Grundriss der Farb. Chemie zum Gebrauch bei Mikroskopischen Arbeiten.*

[3] "Manual of Bacteriology," p. 101.