

## THE MORDANTING ACTION OF METALLIC FERRO- AND FERRICYANIDES<sup>1</sup>

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There has been very little quantitative work done on the mordanting action of metallic salts, probably because workers were in search of a specific result and performed only the experiments which seemed most likely to be successful.

The mordanting action is a function of the nature of the dye, and of the acid and metal united in the mordant, and also probably of the concentration of the ions in the solutions. In some cases there is possibly an effect of exposure to light, *e. g.*, in the silver compounds. As in any dyeing process, the concentration of hydrogen and hydroxyl ions and neutral salt has a very great influence on the result.

With this large number of factors it is easy to understand the contradictory results which have been obtained. These results are also very greatly affected by the physical state of the mordant, *i. e.*, colloidal or crystalline, and are very much complicated in case the mordant is in gelatiné. In order to simplify the problem, the experiments described were conducted in a system containing only water, the mordant, the inorganic salt resulting from the action of the soluble metal and acid salts, the dyestuff, and a slight excess of acid salt to insure uniformity. A control series was run in the case of silver ferrocyanide to determine the effect of the presence and nature of the neutral salt.

Ferri- and ferrocyanides of the heavy metals were chosen for the experiments and the mordanting action of the following ferro- and ferricyanides was studied; cuprous, cupric, silver, zinc, cadmium, mercurous, mercuric, cerous, ceric, thorium, stannous, stannic, lead, vanadium, bismuth, uranyl, manganous, ferrous, ferric, cobaltous and nickelous. The dyes were selected to represent the common groups from the standpoint of chemical classification and a few more were included to represent special characteristics of the organic molecule. The dyes chosen were:

<sup>1</sup> Communication No. 46 from the Research Laboratory of the Eastman Kodak Company.

TABLE I

No.	Name	Constitution	Characteristic
1	Suphanilic acid coupled with Neville and Wintler acid (sodium salt)		acid
2	Tartrazine	Oxy-azo	acid
3	Fuchsine	Pyrazolone (disazo carboxy)	acid
4	Crystal Violet	Triphenyl-methane-triamine	basic
5	Acid Violet 4 BC	Triphenyl-methane-hexamethyltriamine	basic
6	Rose Bengal	Triphenyl-methane acid-tridialkyl-amine	acid
7	Acridine Orange NO	Fluorescein (halogenated)	acid
8	Alizarine Red S	Amino-acridine	basic
9	Tanninheiotrope	Supho-alizarine	acid
10	Capri Blue G-ON	Methylamino-azine	basic
11	Methylene Blue BB	Alkylamino-oxazine	basic
12	Quinoline Yellow	Disulfo-phthalo-quinaldine	acid

Crystal Violet and Acid Violet 4 BC were taken because they represent basic and acid alkylated aminotriphenyl methane dyes. Rose Bengal is an acid dye containing a so-called "basic oxygen" atom.

Since a 5% excess of the acid salts was used, the effect of a large excess of these salts on the dyes was determined. The effect was in most cases inappreciable, and for the one exception noted in the table, it was assumed that the slight action of a 5% excess would not influence the results.

TABLE II

Action of large excess of potassium ferrocyanide and potassium ferricyanide on the dyes

		Ferrocyanide	Ferricyanide
1	Benzenesulphonic-azo N. and W. salt	nil	nil
2	Tartrazine	nil	nil
3	Fuchsin	nil	yellow and vvs. ppte.
4	Crystal Violet	nil	redder
5	Acid Violet 4BC	nil	redder
6	Rose Bengal	nil	yellower
7	Acridine Orange NO	nil	vs. ppte.
8	Alizarine Red S	nil	yellower
9	Tanninheliotrope	nil	yellower
10	Capri Blue GON	nil	greener
11	Methylene Blue BB	nil	partially pptd.
12	Quinoline Yellow	nil	nil

The method of testing the mordanting power consisted in the preparation of a suspension of the insoluble ferri- or ferrocyanide of such molar concentrations as to show clearly the relative mordanting action on the various dyes. This concentration was usually 0.005 *M* but in several cases other concentrations were used for obvious reasons. About 20 cc. were treated in a test tube with three drops of a 5% solution of the dyes selected and the amount of dye in solution after the precipitate settled out roughly determined by comparison with standards.<sup>1</sup>

<sup>1</sup> The tabulation of the experimental data is omitted in order that the presentation may be more concise. It is believed that the tables and conclusions given contain all the data of interest.

### Copper Salts

Ferricyanide mordants better than ferrocyanide and cupric better than cuprous. Cupric ferricyanide distinctly mordants the basic dyes better than the acid. Cuprous ferricyanide is selective, but in general it mordants the basic dyes better than the acid dyes.

### Silver Salts

Silver ferricyanide is a selective mordant for basic dyes as is also the ferrocyanide but is more pronounced in its action. The washed ferrocyanide shows practically the same action as that in excess ferrocyanide, the washed mordant being slightly less active; but in presence of excess of silver ions, there is a pronounced difference. The acid dyes are very completely mordanted, this being the case with only a few of the mordants. This action is not due to the formation of the silver-dye salt because in a comparison series containing only silver ions and dye there was no measurable loss of dye by precipitation of the silver salt. However, the presence of the silver ion tends to cause precipitation of the acid dyes as the presence of excess anion favors the precipitation of the basic dyes.

The silver ferrocyanide turns blue under a white top layer on standing in the test tube. Since silver ferrocyanide is commonly described as being unaffected by light, this discoloration may be due to a trace of adsorbed silver nitrate or silver chloride.

### Zinc Salts

The zinc salts are remarkable in that they exhibit the strongest mordanting power of any of the metal salts. The ferricyanide especially has about ten times the mordanting power of the other metal ferricyanides. An explanation may be a difference in physical state; that is, assuming that the precipitate is much more finely divided, it is to be expected that the dyes would be much more strongly adsorbed than by coarser particles. The zinc salts mordant quinoline yellow

showing that they have much greater mordanting power than the other metal salts.

#### Cadmium Salts

Although cadmium is chemically very closely allied to zinc, it has not the same mordanting power, indeed the cadmium salts are, with two exceptions to be noted later, the poorest of the mordants, the ferricyanide being the better of the two.

#### Mercury Salts

The mercurous ferricyanide is an excellent mordant for the basic dyes but the precipitate is only slightly colored, indicating that the dye may be chemically affected as is the case with mercuric ferricyanide. The action of the mercury salts is more pronounced on basic dyes than on the acid dyes.

#### Cerium Salts

Of the cerium salts, ceric ferricyanide precipitates or destroys nearly all of the dyes. The cerous salts are not of special interest, the ferricyanide not producing precipitates.

#### Thorium Salts

The ferricyanide mordants the basic dyes but the ferrocyanide seems to be a specific mordant for acid dyes. Since thorium ferrocyanide exhibited a strong specific adsorptive power on acid dyes, its action on nearly one hundred and fifty acid dyes was determined in comparison with aluminum chloride, the latter on 1% solutions of the dyes. It was hoped that it would be found a more valuable specific mordant than the aluminum chloride but a few dyes were precipitated by aluminum chloride which were not mordanted from their dilute solutions by the thorium salt. Thus the only practical value of the test would be in cases where only a small amount of dye is available.

#### Tin and Lead Salts

The tin and lead salts do not exhibit any striking characteristics, the ferricyanides being more active than the ferrocyanides.

#### Vanadium Salts

The vanadium salts show colloidal precipitation but the results are not conclusive as the only vanadium salt available was one containing a small amount of oxalic acid.

#### Bismuth Salts

In order to prevent the formation of the oxy bismuth salts, a small amount of hydrochloric acid was added to the solution. The salts are mordants for basic dyes, the ferricyanide being the better.

#### Uranium Salts

The uranium salts show strong mordanting action especially for basic dyes, the action of the ferricyanide being slightly more pronounced.

#### Manganese, Iron, Nickel and Cobalt Salts

The mordanting action of these salts is on the whole comparatively slight. The action is greatest on the complex acid dyes and especially on Alizarine which is in accord with dyeing practice in which salts of these metals are used as mordants. It is remarkable that the ferrocyanide of nickel, otherwise a weak mordanting agent, should mordant quinoline yellow to a slight extent.

#### Silver Halides

The outstanding fact concerning the halogen silver salts is that the mordanting power is very slight. The iodide is the only one which shows effective mordanting, and that only at a concentration three times that used for the other metals.

The numerical tabulation of results is given below. The action is scaled as follows on the basis of 0.005 *M* suspensions.

imperceptible	1
very slight	2
slight	3
pronounced	5
nearly complete	7
complete	10

TABLE III

Metals	Acid Dyes		Basic Dyes		Size of Molecule	
	Ferriyanide	Ferrocyanide	Ferriyanide	Ferrocyanide	Ferriyanide	Ferrocyanide
	Cuprous	3	1	5	1	402
Cupric	4	3	10	2	680	335
Silver (excess cyanide ion)	5	5	10	7	535	630
Silver (excess silver ion)	—	15	—	5	—	—
Silver (washed)	—	5	100	7	619	350
Zinc	8	5	3	2	760	435
Cadmium	2	3	10	10	815	1012
Mercurous	7	5	—	7	1027	812
Mercuric	—	5	5	5	1200	1200
Cerous	3	3	—	7	352	350
Ceric	15	3	10	2	1268	350
Thorium	10	20	10	7	1544	440
Stannous	3	5	7	7	780	450
Stannic	5	2	10	3	1205	330
Lead	3	3	10	1	1220	630
Vanadium	3	2	10	—	263	836
Bismuth	5	5	10	7	420	1465
Uranyl	5	5	7	5	483	1710
Manganous	1	2	3	2	589	300
Ferric	1	3	2	2	600	860
Cobaltous	—	3	—	2	—	320
Nickelous	2	3	2	2	600	320
Silver chloride	2	5	2	1	611	330
Silver bromide	—	0	—	0	140	—
Silver iodide	—	1	—	1	190	—
				2	235	Halides

The average mordanting power of each metal (obtained from the table) if placed in the periodic table instead of the atomic weight shows a systematic relation between mordanting power and position in the table. The high valent high atomic weight metals form ferro- and ferricyanides whose mordanting power is very great. The irregularities are probably due to difference in physical state of subdivision which enters as a secondary effect.

TABLE IV  
Periodic Classification

Na	Mg	Al	C	N	O	F			
Cu	Zn			V	Cr	Mn	Fe	Ni	Co
6	30			5		2	2	2	2
Ag	Cd		Sn						
8	2		6						
	Hg	Ce	Pb		Bi				
	8	6	5		7				
		Th				U			
		10				6			

## Conclusion

Three general conclusions may be drawn:

(1) All ferricyanides mordant basic dyes better than acid dyes in the presence of a slight excess of ferricyanide ion.

(2) All ferrocyanides with the exception of thorium and lead mordant basic dyes in the presence of excess ferrocyanide ion. In the case of lead there is the possibility of the presence of a basic salt which would explain the abnormality. In the case of thorium the high molecular weight of the ferrocyanide may be the explanation, though it is probable that the presence of the heavy multivalent ion (which tends to precipitate the acid dyes) is the more logical explanation.

(3) Ferricyanides mordant better than ferrocyanides. On inspection of the table of relative mordanting powers, the metals are seen to fall into certain natural groups.

I. Manganese, cobalt, iron, nickel and the silver halides show practically no mordanting action. The explanation in the case of the halides is possibly the low molecular weight;

if equal weights of the iodide and ferrocyanide were taken, the action would probably be of the same order of magnitude, but the bromide and chloride would still be abnormally inactive.

II. Cadmium, cuprous, cerous, stannous and

III. Cupric, stannic, lead, vanadium, bismuth, uranium and ceric form intermediate classes.

IV. The heavier metals silver, mercury and thorium are the strongest mordants.

An attempt to connect the mordanting power with the molecular weight of the mordant is only partially successful. That there is such a definite connection is indicated by the extremely light (silver halide) and extremely heavy (cerium, thorium, tin, lead, bismuth, uranium) molecules but this is at least partially masked by the physical state. It is practically the same method of expression as the periodic system.

The work has shown definitely that mordanting power in the presence of slight excess of cyanogen compound is primarily a function of the molecular weight and valence of the metals. Secondary factors are the physical state of subdivision and molecular weight of the mordant. It is probable that the nature of the adsorption complex varies in most cases with the ionic concentration in solutions.

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## NEW BOOKS

*Annual Reports of the Society of Chemical Industry on the Progress of Applied Chemistry. Vol. I (1916). 21 × 15 cm; pp. 335. London: Harrison & Sons, 1917. Price: 5/6.*—This is the first volume of what should be a very valuable series of annual reports on progress in applied chemistry. The volume does not cover the whole ground because the compilers of the sections on fibers, dyeing, metallurgy, electrochemistry and sugar were unable to finish their manuscripts in time. For obvious reasons no report on explosives will be made for the present. The separate articles are entitled: fuel and heating; gas—destructive distillation—tar products; mineral oils; coloring matters and dyes; acids, alkalies, salts, etc.; glass and ceramics; building materials; oils, fats, and waxes; paints, pigments, varnishes, and resins; india-rubber, etc., leather and glue; fermentation industries; water purification and sanitation; fine chemicals; medicinal substances, and essential oils; photographic materials and processes.

There is an interesting paragraph on the low temperature distillation of coal, p. 39. "Probably in no other department of the industry is research so much required as upon this question of distillation at low temperatures, and an investigation of this nature would profit by the experience of the gas engineer and chemist. A perusal of recent gas literature creates an impression that the proposition is generally received with antipathy. This attitude may have arisen as a result of the failure of earlier attempts promoted too exclusively by the financier. The fact remains, however, that raw coal should be treated, prior to its use for industrial and domestic purposes, for the extraction of valuable carbonaceous compounds, ammonia and sulphur. The richer hydrocarbons produced during the combustion of coal which are recovered by this process cannot, in most cases, be adequately utilized in existing appliances, and disappear as smoke. The adoption of such a process may solve the problem of the shortage of ammonia in the United Kingdom. An investigation of this nature is one which gas engineers and chemists are eminently competent to undertake, and, moreover, the interests of gas undertakings as purveyors of gaseous fuel need not be affected by the additional responsibility of preparing solid fuel; in fact, in the combination of the two processes appears to lie the ultimate scientific solution of the problem."

On p. 53 there is a brief discussion of the coking property of coal. "The property in coal of forming coke appears to depend upon the presence of constituents which melt at a lower temperature than that at which the rate of decomposition or carbonization becomes rapid. Certain of these constituents are readily oxidized, and this property is considered to account for the fact that the coking property of coals is diminished by exposure to air. By heating coal in an inert atmosphere for several hours at 300° C, the coking power of some coals is destroyed and of others weakened. The true coking coals appear to retain sufficient resin-like bodies after being heated to about 300° C to yield the necessary fusible material to form coke when heated to 320° C or above. Feebly coking coals yield a similar fusible body, but the quantity is insufficient to melt or render liquid the whole of the material, and coke is not formed.

"Investigators are in agreement that the true coking coals in addition