ENGLISH INKS: THEIR COMPOSITION AND DIFFERENTIATION IN HANDWRITING.

BY C. A. MITCHELL, B.A., F.I.C.

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IN the following paper I have dealt chiefly with the differentiation of inks, more especially when forming the dried pigment in handwriting; and as I wished to describe characteristic reactions given by the products of the manufacturers whom I have named, I have purposely refrained from drawing conclusions as to the relative merits of the various preparations.

In the old type of iron-gall inks—those in which partial oxidation was made to take place before bottling—there could not have been very marked differences, except such as would result from the use of varying proportions of galls, ferrous sulphate, or gum. Hence, as a rule, it would have been practically impossible to distinguish with any degree of certainty between the characters made by two such inks.

This old type of ink is now rarely met with, having been all but superseded by the modern unoxidised inks, in which a "provisional" colouring matter is introduced to give some colour to the writing, pending the formation of the black insoluble tannate within the fibres of the paper.

It is true that added dye-stuffs were sometimes employed to improve the colour of inks of the old type, and the use of indigo for this purpose is mentioned by Eisler (1770); and of logwood by Lewis (1763); but the inks themselves were still more or less oxidised before use, and it was not until early in the nineteenth century that indigo or logwood was used for their modern purpose of rendering the writing immediately visible. Alizarine was also employed as a provisional colouring matter in Germany, and although it soon gave place to indigo, the unoxidised inks into which it was introduced have retained their original name of "alizarine inks" to the present day.

The discovery of the aniline dye-stuffs added largely to the provisional colouring matters at the disposal of the ink-manufacturer, and such dyes are now found in most of the blue-black inks of to-day.

There is a considerable variation in the proportion of solid matter and of iron to organic matter in commercial writing fluids, as will be seen in the following table, giving the results of partial analyses made during the past twelve months of the best-known preparations. Most of these are iron-gall inks, but the list also includes samples of chrome-logwood and aniline inks. I take this opportunity of thanking those manufacturers who have kindly placed specimens of their preparations at my disposal.

I.—COMPOSITION OF ENGLISH WRITING INKS.

Ink.	Specific Gravity at 15° C.	Water per Cent.	Total Solids per Cent.	Mineral Matter (Ash) per Cent.	Iron per Cent.
Arnold's Blue-black	1·0216	96·35	3·65	0·94	0·25
Blackwood's Blue-black	—	96·82	3·18	0·77	0·28
,, "Record"	—	92·06	7·94	1·40	0·59
Carr's Blue-black	1·0220	96·01	3·99	1·07	0·29
,, Black	1·0244	95·84	4·16	1·39	0·48
Day and Martin's Blue-black ...	—	92·25	7·75	2·52	1·09
Draper's "Dichroic"	—	95·16	4·84	1·10	trace
Faber's Blue-black	1·0205	95·58	4·42	1·22	0·49
,, Black	1·0153	96·66	3·34	0·82	trace
Field's "Non-corrosive"	1·0121	97·55	2·45	0·64	0·28
Halsey's Blue-black	1·0208	95·34	4·66	0·54	0·28
Lyon's Blue-black	1·0239	95·14	4·86	1·01	0·35
Mordan's "Azuryte"	—	95·94	4·06	0·86	0·29
,, Blue-black	1·0225	95·54	4·46	0·62	0·18
,, "Jet-black"	1·0256	94·04	5·96	0·99	0·21
Morrell's Blue-black	1·0276	95·16	4·84	1·66	0·56
Paul's Blue-black	—	96·12	3·88	0·97	0·33
,, Black	—	96·68	3·32	2·28	trace
Pridge's Blue-black	1·0499	92·22	7·88	1·88	0·84
,, Black	—	92·32	7·70	1·42	0·49
Stephens' Blue-black	1·0206	96·21	3·79	0·76	0·32
Vicker's "Penwing"	—	98·11	1·89	0·42	trace
Walkden's Blue-black	1·0221	95·58	4·42	0·72	0·22
,, Black	1·0293	94·39	5·61	1·12	0·36

These results show that, notwithstanding the probably closely similar methods of preparation, there are yet wide variations in the composition of the different inks. Thus, the total amount of solid matter (dried at 100° C.) ranges from 1·89 to 7·94 per cent., the ash from 0·42 to 2·52 per cent., and the iron in the iron-gall inks from 0·18 to 1·09 per cent.

From time to time during the past five years I have examined samples of several of the different kinds of inks mentioned in the table, and the results indicate that the composition of an individual preparation by the same manufacturer remains fairly constant.

I have been unable to devise any satisfactory method of estimating gallotannic acid and allied substances present in ink. A method of absorption by means of hide powder might yield satisfactory results if gallic acid were not also a usual constituent. On the other hand, the "provisional" colouring matter in inks interferes with the estimation of the gallotannic and gallic acids together by the colorimetric method which I devised for the valuation of tannin materials for ink-making ("Inks and their Manufacture," p. 85).

The tannin in freshly-prepared ink appears to be in the form of a soluble iron tannate, which slowly oxidises on contact with air, forming an insoluble tannate. I have frequently examined the deposit which forms when a solution of gallotannic acid and ferrous sulphate is allowed to stand in contact with the air, and have found that when washed with cold water and dried at 100° C. it yields from 7·8 to 8·8 per cent. of ferric oxide, corresponding to 5·4 to 6·2 per cent. of iron. Of the known insoluble iron tannates, the one that corresponds best with this proportion of iron is that described by Wittstein (*Jahresber. der Chem.*, 1848, **28**, 221) and by Schiff (*Ann. Chem. Pharm.*, 1875, **175**, 176), which contains 5·53 per cent. of iron, and has the formula—

$$\begin{array}{l} Fe\ (C_{14}H_9O_9)_3 \\ | \\ Fe\ (C_{14}H_9O_9)_3. \end{array}$$

If, as seems probable, this is the tannate formed in the gradual darkening of ink upon paper, any excess of iron or gallotanic acid beyond the quantities required to form this compound should be unnecessary, or even injurious, to the permanence of the writing.

The dye-stuffs in the blue-black inks referred to in Table I. varied in colour from pale greenish-blue to indigo and deep violet, and no two gave identical reactions—at all events, when mixed with the iron tannate to form the pigment in writing. It is mainly owing to these differences that it becomes possible to distinguish between the handwriting done with different kinds of ink, and in some cases it is not even necessary to apply chemical tests for the purpose.

Thus, in the case of words written with inks having respectively an azure blue and an indigo colour while wet, it is easy to distinguish the colours under the microscope months after the writing has attained its maximum intensity.

In examining writing to determine whether it has been done with a particular ink, it is advisable to prepare a colour scale with that ink, consisting of four washes ranging from the faintest to the darkest possible tone, the paper being left for at least twenty-four hours. The scale is then compared under the microscope with different parts of the writing in question, and is subsequently used in comparative chemical tests when such are permissible. The broad surfaces of colour are comparable with the surfaces of the written characters as seen under the microscope, and there is thus obtained what practically amounts to a magnified record of the microscopical appearance.

Lovibond's tintometer will also be found useful in comparing different specimens of handwriting and matching the colours obtained in chemical reactions with those given by the colour scales prepared from known or suspected inks.

With regard to the use of photography as a means of differentiating inks in writing, I have made numerous experiments with colour-sensitive plates and screens, but find that the differences of intensity shown in the negatives are no greater than may be seen with the naked eye. I am, therefore, unable to confirm Minovici's (*Bull. della Soc. Fotografia Ital.*, 1900, **12**, 349) experience in this respect.

For the differentiation of inks in handwriting by chemical methods a wide choice of reagents is available, but those I have used will, as a rule, be found sufficient, viz.:

1. Hydrochloric acid (5 per cent. solution).
2. Oxalic acid (5 per cent. solution).
3. Stannous chloride (10 per cent. solution).
4. Nascent hydrogen (50 per cent. HCl with zinc).
5. Bromine (saturated aqueous solution).
6. Bleaching powder (saturated solution).
7. Titanous chloride (the impure commercial solution).
8. Potassium ferrocyanide (5 per cent. solution containing 1 per cent. of HCl).

Of these reagents, the two first act mainly upon the iron tannate, and leave the provisional colouring matter. The third and fourth bleach the iron tannate, and reduce the provisional pigment, changing its colour. The fifth and sixth reagents may act on both pigments, causing more or less superficial bleaching. The titanous chloride solution is a powerful reducing agent towards both pigments, whilst the acidified ferrocyanide solution acts mainly upon the iron liberated from the iron tannate.

In the table on p. 84, showing the reactions given by my samples of commercial inks, the reagents were applied by means of a brush, and the writing examined under the microscope both by reflected and by transmitted light, first after five minutes', and again after twelve hours', exposure to the air. The colorations which appeared upon the wrong side of the paper were sometimes also very characteristic, especially in cases where there had been superficial bleaching. In the tests with titanous chloride, blotting-paper was applied after the lapse of five minutes.

I had recently to decide whether two specimens of handwriting were in the same ink and were done at one and the same time. The first question was easily solved, but from the results of my experiments I found that it was not possible to distinguish between inks after they had attained their maximum degree of intensity, or until after the provisional colour had begun the fade.

It is, as a rule, possible to distinguish colorimetrically between freshly written and old writings up to about the sixth day, after which the iron tannate has become almost completely oxidised, and differentiation is no longer possible until after the lapse of a year or more, according to the degree of permanency of the provisional pigment.

As a rule, the pigments employed offer greater resistance to the action of chemical reagents, but are infinitely less stable than iron tannate when exposed to the action of light and air, and eloquent testimony to this difference is given by a comparison of certain manuscripts of the seventh and eighth centuries with type-written documents which have been put aside for a year or two.

II.—Reactions given by English Inks in Handwriting.

Inks.	Hydrochloric Acid, 5 per Cent.		Oxalic Acid, 5 per Cent.		Stannous Chloride, 10 per Cent.		Nascent Hydrogen.		Bromine (Aqueous Solution).		Bleaching Powder.		Titanous Chloride.		Potassium Ferrocyanide, 5 per Cent., +HCl, 1 per Cent.	
	Moist.	Dry.	Moist.	Dry.	Moist.	Dry.	Moist.	Dry.	Moist.	Dry.	Moist.	Dry.	Moist.	Dry.	Moist.	Dry.
Arnold's Blue-black	greenish-blue	green-blue	green-blue	green-blue	blue-violet	lilac	violet	violet	deep violet	violet-black	greenish	surface bleaching	dirty green	green-brown	bright green-blue	green-blue
Blackwood's Blue-black	bright blue	blue	bright blue	blue	bright blue	violet	bright blue	violet	deep blue	blue	deep blue	deep blue	green-blue	green-brown	bright blue	blue
,, "Record"	gray	gray	light gray blue	pink-gray blue	gray	yellow-gray	nearly bleached violet	pale pink violet	little action	smudged	slight bleaching	little change	light orange	orange	green-black	green and black
Carr's Blue-black	dark blue	dark blue			purple-blue	deep violet			dark blue black	dark blue	slight bleaching	blue-gray	blue-gray	olive-green	deep blue	deep blue
,, Black	darkened	violet-gray	gray	gray-violet	blue-gray	violet-gray	blue-gray mauve	blue-gray mauve		violet-black	gray-black	slight bleaching	dark brown	brown	deep blue	deep blue
Day and Martin's Blue-black	deep blue	deep blue	gray-blue	green-blue	deep blue	deep violet			deep blue	deep blue	nearly black	gray and black	dark gray-blue	yellow-brown	nearly black	deep blue
Draper's "Dichroic"	deep violet	deep violet	red-violet	red-violet	violet	mauve	violet	pink-violet	violet-black	violet-black	yellow on violet	yellow on violet	deep maroon	rose-brown	deep violet	green-violet
Faber's Blue-black	light blue	blue	bright blue	bright blue	bright blue	light blue	bright blue	green-blue	bright blue	blue with black patches	deep blue, some bleaching	blue with light patches	green-blue	orange	bright blue	green-blue
,, Black	purple	deep violet	purple	pink	purple	violet	red-purple	red-violet	deep purple	deep violet	deep purple, some bleaching	yellow over violet	purple-brown	rose-brown	deep purple	rose-brown
Field's "Non-corrosive"	deep blue	deep blue	deep blue	deep blue	violet-blue	deep violet	violet	violet	deep blue	deep blue	surface bleaching	yellow on blue	navy blue	yellow-brown	blue	green-blue
Halsey's Blue-black	bright blue	bright blue	blue	green-blue	violet-blue	violet-blue	violet	violet	darkened	dark blue	surface bleaching	yellow on blue	blue-gray	gray	green-blue	light green-blue
Lyon's Blue-black	deep blue	bright blue	bright blue	bright blue	blue	bright blue	blue	violet-blue	dark blue	dark blue	slight bleaching	green-gray, black spots	deep blue	dark olive-green	deep blue	deep blue
Mordan's "Azuryte"	bright blue	blue	bright blue	bright blue	bright blue	bright blue	bright blue	bright blue	dark purple	dark purple	slight bleaching	nearly black	dark green-gray	green-brown	dark blue	dark blue
,, Blue-black	bright blue	blue	bright blue	bright blue	bright blue	bright blue	blue	blue	darkened	purple-black	bleaching	gray and black	deep green	brown	deep blue	deep blue
,, "Jet-black"	darkened	blue-gray	gray	gray	light gray	light gray	light gray	light blue-gray	darkened	blue-gray	darkened	blue-gray	light brown	red-brown	green-gray	green-gray
Morrell's Blue-black	bright blue	bright blue	bright blue	bright blue	violet-blue	deep violet	violet	deep violet	deep blue	deep blue	slight bleaching	deep blue	deep green-blue	dark olive-green	indigo-blue	blue
Paul's Blue-black	light blue	blue	bright blue	bright blue	bright blue	bright violet	light blue	light violet	deep blue	deep blue	deep blue	deep blue	green-gray	yellow-brown	bright blue	blue
,, Black	deep blue	violet-black	deep blue	green-gray	rose, then bleach'd	cream	deep violet-blue	violet-gray	blue, some bleaching	gray	bleached	fawn stain	bleached	dirty yellow	deep blue-black	black
Pridge's Blue-black	bright blue	green-blue	bright blue	pale blue	light green-blue	pale mauve	bright blue	blue	deep blue	nearly black	deep blue	nearly black	olive-green	yellow-brown	deep blue	green-blue
,, Black	blue	dull blue	green-blue	gray-blue	light green-blue	blue-gray	light green-blue	gray-violet	dark blue	very dark blue-gray smudge	dark blue	dark blue, gray smudge zone	yellow-gray	olive-brown	green-blue	blue-green
Stephens' Blue-black	deep blue	green-blue	deep blue	green-blue	violet	lilac	violet-blue	mauve	slight bleaching	deep blue	surface bleaching	yellow on blue	nearly black	brown	deep green-blue	green-blue
Vicker's "Penwing"	reddened	pink-brown	pink-violet	red-pink	blue-violet	pink	pink-violet	red-pink violet	surface bleaching	yellow and black	surface bleaching	yellow and black	maroon	violet-black	deep violet-black	pink-brown
Walkden's Blue-black	bright blue	bright blue	blue	light blue	bright blue	bright violet	blue		blue	gray-blue	surface bleaching	deep blue	gray-blue	purple-gray	dark blue	blue
,, Black	blue-black	blue-black	gray-violet	gray-violet	violet-black	gray-violet	gray-violet	gray-violet	blue black	blue-black	nearly black	black	green-gray	gray-brown	green-black	blue and black

DISCUSSION.

Mr. E. R. BOLTON asked if the author had made any use of starch-grain plates in his photographic experiments.

Mr. CHAPMAN said that in determining tannin in hops, he had found it satisfactory to precipitate the tannin as cinchonine tannate. Possibly in the case of inks also that method might be useful for the separation of the tannic acid from the gallic acid, as cinchonine tannate was very insoluble, whereas the gallate was soluble. It was perhaps not very widely known that titanous chloride was now a comparatively cheap reagent. The ordinary solution to which Mr. Mitchell had referred contained a little lead, but otherwise was tolerably pure, while the perfectly pure salt was not prohibitively expensive. It was a very useful reagent in the estimation of iron, etc., being a much more powerful reducing agent than stannous chloride.

The PRESIDENT asked if the author knew of any black or blue-black ink that was absolutely indelible to ordinary bleaching agents. He himself had never met with one capable of resisting the action of potassium permanganate followed by sulphurous acid.

Mr. MITCHELL, in reply, said he did not know of a blue-black ink that would withstand any powerful bleaching agent. Certain type-writing inks which were impregnated with fine carbon might be taken as practically permanent in this respect, and all the so-called "safety" inks contained such an admixture of carbon. A thoroughly well-made iron-gall ink, however, would be permanent for eight or ten centuries, and in Germany the use of such inks for official documents was insisted upon. With regard to photography, he had used only ordinary and Cadett spectrum plates, with the "absolutus" screen, and here, as he had said, no greater difference in intensity was obtained than was apparent to the naked eye. The method suggested by Mr. Chapman for the estimation of gallo-tannic and gallic acids did not overcome the difficulty caused by the provisional colour.

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