UTILISATION OF MYROBALANS.

PART III. UTILISATION OF MYROBALAN EXTRACT FOR THE PREPARATION OF INK AND FOR COTTON DYEING.

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INKS.

Myrobalans have been used for centuries for making ink. The myrobalans are soaked in water and allowed to ferment, and the required quantity of either iron filings or ferrous sulphate added, and after filtering through cloth, indigo or any other suitable blue or black dye is added and allowed to settle for a number of days before the ink is ready for use.

Earliest mention of the possible use of myrobalans as a substitute for galls is that made by A. Johnson (*Trans. Soc. Arts,* 1801, **19**, 343), in which he stated that the natives of India used them for giving a black colour to leather, mixing the powder with iron filings and water.

Schiff (*Ann. Chem. Pharm.*, CL, 164) attributed the property possessed by gallic and tannic acids, of forming blue compounds with ferric salts to the presence of free phenoloid hydroxyl groups. Thus when a coloration is obtained with ferric salt, the presence of a free hydroxyl group may be inferred. Schiff came to the conclusion that the intensity of the colour is proportional to the number of free hydroxyl groups; the substances having one free hydroxyl group give violet coloration, while if they contain several free hydroxyl groups, deep blue-black coloration is produced.

Schluttig and Newmann (*Die Eisengallius Tinten,* 1890, **16**) further investigated the question of the formation of permanent inks on vegetable fibres and came to the conclusion that the compound must contain three hydroxyl groups in adjacent positions in order to yield colours forming a permanent ink on paper. For instance, hydroquinone $C_6H_4 <^{OH}_{OH}$ does not yield an ink while gallic acid $C_6H_2 <^{OH}_{OH}{}_{COOH}$ gives permanent coloration.

They also showed that ink made with gallic acid produces writing that darkens more than that produced by ink made with other phenolic materials that give coloured compounds with ferric salts. Since the amount of gallic acid recommended by them for preparing a litre of ink was larger than what would dissolve in a litre of water, gallo-tannic acid was added to make up the difference. When the myrobalan infusion is allowed to ferment gallic acid is produced, which yields deep blue-black coloration with iron salts on exposure to air.

In our investigations, we have used the formula recommended by the U.S. Government for standard writing ink (Federal specification TT—1–563, Ink) as given below:

	Writing ink	Record ink
Tannic acid	11·7 gms.	23·4 gms.
Gallic acid	3·8 ,,	7·7 ,,
Ferrous sulphate $FeSO_4$ 7 H_2O ..	15·0 ,,	30·0 ,,
Hydrochloric acid 2 : 1 ..	12·5 ,,	25·0 ,,
Carbolic acid	1·0 ,,	1·0 ,,
Dye	3·0 ,,	3·5 ,,
Water to make	1 litre	1 litre

Inks were prepared with the following tannic acids: (1) Riedel and Haen's pure gallotannic acid, (2) Baird and Tatlock's pure gallotannic acid, (3) myrobalan extract, (4) myrobalan tannic acid prepared by precipitation with lead acetate, (5) E. Merck's commercial gallotannic acid, keeping the amount of gallic acid same and were tested for stability. The results are given in the following table:

No. of the inks	11	12	13	14	21	555	41	41·5	51
Sources of tannic acid	R.H.	R.H.	R.H.	R.H.	B.T.	Merck	(3)	(3)	(4)
Tannic acid	11·7	23·4	11·7	11·7	11·7	11·7	11·7	17·5	11·7
Gallic acid (gms.)	3·8	7·6	3·8	3·8	3·8	3·8	3·8	3·8	3·8
Ferrous sulphate $FeSO_4$ 7 H_2O (gms.)	15·0	30·0	15·0	..	15·0	15·0	15·0	15·0	15·0
Ferrous ammonium sulphate (gms.)	..	..	..	42·1	..	..	..	..	..
Hydrochloric acid dilute (gms.) ..	12·5	25·0	12·5	12·5	12·5	12·5	12·5	12·5	12·5
Phenol (gms.)	1·0	1·0	1·0	1·0	1·0	1·0	1·0	1·0	1·0
Dye (gms.)	3·5	3·5	3·5	3·5	3·5	3·5	3·5	3·5	3·5
Gum (gms.)	..	..	2·5	..	..	..	..	..	..
Water to make	1000 c.c.								
Stability in days to form sediment	practically no sediment for 6 months					8	8	10	10
Washing and Fading tests with water	not affected at all					slightly washed		not affected	
Washing and Fading tests with alcohol	do.					do.		do.	

After maturing for one month and decanting, all inks except Nos. 555 and 41 were stable for six months without any formation of sediment.

The corrosive properties of inks are obviously proportional to the hydrogen-ion concentration. Owing to the difficulty of measuring pH of inks by the ordinary methods, we resorted to the measurement of electrical conductivity which has been recently found by Karoly Ipolyi (*Amer. Chem. Abs.*, 1937, 31, 2455) to be proportional to the corrosive properties, conductivity being mainly due to hydrogen ions.

Measurements of electrical conductivity were carried out by using a Leeds and Northrup conductivity apparatus. The measurements were made at 30° ± 0.02°. Cell constant was obtained in the usual manner using N/10 solution of potassium chloride.

In addition to the above inks, four commercial inks were taken for comparison: (1) Stephen's blue black writing fluid, (2) Swan blue black ink for fountain pens, (3) Quink ink manufactured by Parker Pens, Ltd., U.S.A., (4) Inkotine manufactured by G. S. Ranade, Bombay. The results are given in the following table:

Ink No.	Conductivity $\times 10^{+2}$	Ink No.	Conductivity $\times 10^{+2}$
11 ..	1·84	51·0 ..	1·91
12 ..	3·06	41·5 ..	2·00
13 ..	1·80	42·0 ..	1·97
14 ..	3·67	Stephen's ink ..	1·88
21 ..	1·88	Swan ..	1·64
555 ..	2·02	Quink ..	1·70
41 ..	1·80	Inkotine ..	1·15

The remarkably low conductivity of Inkotine is worth noting. The inks prepared from myrobalan extract and purified myrobalan tannic acids are comparable with the foreign made inks regarding corrosive property, and are also satisfactory towards washing and fading tests.

Utilisation of Myrobalans in Cotton Dyeing Industry.

A number of tanning materials are used as mordants in the dyeing of cotton and linen. Some of the substances are used on account of their cheapness, instead of pure tannic acid, in mordanting. Among

the tannin materials myrobalans and sumach are valued next to gallo-tannic acid, then follow valonia, divi-divi, knoppern, chestnut, etc.

In addition to their use as mordant, myrobalans are used for the weighting of silk.

Three methods for evaluating tannins for dyeing purposes were used. (1) Becker's method (*Chem. News*, Vol. **L** 1, p. 229). (2) Examination of tannins by dye-trials. (3) Actually mordanting and dyeing with methyl violet and malachite green.

The materials used were:—*I. Tannins*: (1) Pure tannic acid ("Kahlbaums"), (2) pure untreated solid myrobalan extract prepared on semi-commercial scale, (3) tannic acid from myrobalans prepared by fractional precipitation with lead acetate, (4) commercial tannic acid (E. Merck's) "Kutub Minar" Brand No. 555, which is used and favoured by almost all dye-houses for mordanting in cotton dyeing in India; *II. Yarn*: 20's count, single unbleached, boiled with soda and then washed with water thoroughly, in order to remove grease and size, was used in all experiments; *III. Fixing Agent*: Tartar emetic was used as a fixing agent after mordanting with tannin; *IV Dyes*: Basic ferric sulphate, methyl violet and malachite green.

All the four samples of tannic acids were analysed both by hide-powder method and by Lowenthal's volumetric method. The latter method gave always slightly lower values than the former.

In the case of E. Merck's commercial tannic acid, the percentage of soluble non-tannins is very high (61.0%). The ash content was found to be 17% and on analysing, tests for magnesium, sodium and sulphate and sulphite ions were obtained.

In evaluating different tannins for their utility in mordanting in the dyeing industry and with the object of investigating their mordanting power, and hence indirectly their tannin content, the experiment was carried out with the Becker's methyl violet precipitation method. The results are tabulated below:

	Experiment Numbers			
	1	2	3	4
Tannin % by dye precipitation method ..	95	52·7	62·08	24·1
,, ,, Hide-powder method	95	55·0	64·0	26·0
,, ,, Lowenthal's method	..	53·4	62·6	24·3

It will be seen from the above that the percentages of tannins obtained by the dye-precipitation method and by Lowenthal's oxidation method agree fairly well. This was next confirmed by making dye-trials.

After estimating tannins by the hide-powder method, Lowenthal's volumetric method and dye-precipitation method, the results were checked by carefully conducted dye-trials as described below:

Amount of tannins taken in each case was 0.2 grams in 200 c.c. of water for 10 grams of unbleached cotton yarn. Temperature of the tannin bath, at the time of introduction of the yarns, was kept constant at 86° C. and then allowed to cool during three hours. The yarns were squeezed, introduced into basic ferric sulphate bath, each one separately and worked for 20 minutes, after which it was washed and dried.

The shades obtained were dark grey and practically of uniform depth which proves that the tannin contents determined by analysis by volumetric method and by dye-precipitation method, are in good agreement with those found by dye-trials. In the case of the myrobalan extract, the hanks, after mordanting with tannins, became slightly yellowish and with commercial tannic acid (Merck's) there was hardly any change.

Actual dyeing with basic dyes.—The dyes used were methyl violet and malachite green. The hanks were mordanted exactly in the same way as described above with the same quantities of tannins. After mordanting, the hanks were squeezed and tannins were fixed by means of tartar emetic (0.1 gm. for 10 gm. of yarn) at room temperature for 20 minutes. The hanks were squeezed, washed well and then dyed with the dyes. Both the above dyes were dissolved in water with the addition of little acetic acid and the solutions made up to known volumes; quantities of above solutions corresponding to 2 oz. per 100 lb. of yarn were used.

On dyeing and washing in cold water once, it was found that the shades obtained with methyl violet were of the same depth, but in the case of malachite green, the hanks mordanted with the original myrobalan extract were affected by the yellow colour of the tannin used. For medium and heavy shades the yellow colour does not interfere with the shades obtained.

SUMMARY.

The properties of inks made with myrobalan extract and purified myrobalan tannic acids have been studied from the point of view of corrosion, stability, washing and fading tests. The results compare favourably with the properties of the well-known inks on the market.

The use of myrobalan tannic acids as mordants for dyeing has been studied. The yellow colour of the acids makes them unsuitable for bright shades but does not affect the medium and the deep shades.

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