THE ANALYST.

SEPTEMBER, 1896.

PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS.

COMMERCIAL PRUSSIAN BLUE.

BY ERNEST J. PARRY, B.Sc., F.I.C., AND JOHN HENRY COSTE, F.I.C.

(Read at the Meeting, June 3, 1896.)

IN G. Hurst's well-known book, "Colours, Oils, and Varnishes," a scheme for the analysis of colours containing Prussian blue is given as follows: "A known weight of the sample should be boiled in caustic soda until the blue is completely decomposed. The mixture is then filtered and the brown residue well washed with hot water until it is quite free from alkali. Next, it is treated with hydrochloric acid until the brown oxide of iron has been dissolved. Lastly, it is filtered, and to the filtrate is added ammonia in slight excess. The precipitate of oxide of iron thus formed is filtered off, washed with water, dried and burnt in a crucible, and then weighed. *The weight of the oxide of iron multiplied by 2.212 gives the amount of Prussian blue in the sample taken.*"

As a matter of fact, under these conditions Prussian blue yields about 28 per cent. of Fe_2O_3 , so that estimations based on Hurst's statement would fall short of the truth by at least 35 per cent. Hurst is here evidently under the impression that all the iron in the pigment is precipitated by treatment with alkali, whereas, of course, all in the form of iron-cyanogen radicle is lost in the filtrate as alkaline ferrocyanide.

The following is given as the complete analysis* of a sample of Chinese blue, one of the best varieties of Prussian blue:

Water	...	...	...	4.487
Oxide of iron	...	...	...	52.055
Cyanogen	...	...	...	43.508
				100.000

The method here employed is evident. Briefly, we presume it involves the determination of the moisture and the ash. Since the pigment contains no oxygen, even if the ash were entirely oxide of iron, the iron present is only 70 per cent. of the amount of oxide, and the cyanogen, evidently taken by difference, would be correspondingly higher.

We have found, and Dr. Williamson† in every case found, that alkali was present in so-called Prussian blue, not merely as alkaline salts not washed away completely, but as an integral part of the cyanide. This alkali does not figure in the above analysis.

* These figures add up to 100.05, evidently by a clerical error.

† *Chem. Soc. Mem.*, 1845-46, 125.

As we are frequently called upon to examine commercial samples of Prussian blue, and of pigments containing this substance, we have considered it desirable to make a more complete examination than the method given above would afford of specimens of blue of known origin, with a view to getting some more definite data for basing conclusions as to the purity of samples of unknown make.

It appeared to us that, more especially in the case of complex pigments ground in oil, the determination of the nitrogen would give valuable information as to the amount of Prussian blue present.

Dyer has shown (*Chem. Soc. Jour.*, 1896, 811) that ferrocyanides and ferricyanides yield the whole of their nitrogen as ammonia when treated by the Kjeldahl-Gunning-Arnold method. We found that potassium ferrocyanide boiled with sulphuric acid for a few minutes gave up all its nitrogen as ammonia. A determination of the water of hydration (lost at 180° to 200° C.) was also made. The results were:

			Found.	Theory.
N	...	...	19.64	19.95
H ₂ O	...	...	12.79	12.71

We therefore felt justified in assuming that equally correct results would be obtained in the case of the allied compounds contained in commercial Prussian blue, an expectation which was fully justified by the agreement of the nitrogen determinations with the other figures obtained.

The following is briefly the scheme of analysis adopted by us:

The moisture is determined at 100°. The water of combination—if the term is here justifiable—can scarcely be determined unless the blue is “burned” and the water collected, as we made several attempts to drive off the water in a current of hot air, gradually raising the temperature until at 230° C., when water appeared to be still coming off, the pigment was decomposed with the formation of ferric oxide. Dr. Williamson, in his classical paper, “On the Blue Compounds of Cyanogen and Iron,”* determined the total water in these pigments by combustion with plumbic chromate. This is apparently the only way of obtaining a correct result, as, on heating, part of the hydrogen is evolved as hydrocyanic acid, the oxygen of the water going to form ferric oxide, as stated. The nitrogen was determined as above described, and was found to differ within small limits. A weighed quantity was ignited, care being taken that the temperature was sufficiently high to decompose the last traces of the blue, but not too high to render the oxide of iron difficult of solution. It is necessary to ensure the complete oxidation of the finely-divided iron, as otherwise it is very difficultly soluble in hydrochloric acid.

In all cases on adding acid to the “ash,” a marked effervescence showed that alkaline carbonate (from the alkali-containing ferrocyanide) was present. Pure blue leaves an “ash” completely soluble in hydrochloric acid, but in the case of adulterated Prussian blue or of diluted blues, barium sulphate or other insoluble matter must be filtered off and weighed before precipitating with ammonia. The iron in the (weighed) mixed oxides was determined by titration with potassium bichromate after reduction with stannous chloride, the alumina being of course estimated by difference. A portion of the filtrate was evaporated to dryness, and, after volatilization of the ammonium salts, the alkaline salts were weighed, and the chlorine therein

* *Loco citato.*

determined by titration with silver nitrate. In another portion of the filtrate the sulphuric acid was determined, and from these data—viz., the weight of the alkaline salts, chlorine, and sulphuric acid—we were enabled to show that in all cases the alkali-metal was almost entirely potassium or sodium, and in no case a mixture of the two metals. Another weighed quantity of the pigment was boiled for a few minutes with aqueous potash, and the resulting precipitate of oxide of iron weighed, after ensuring its complete conversion into Fe_2O_3 . This, multiplied by 0.7, represents the “extra radicle” iron.

The following tables represent the composition of eight samples of blue sold by makers of repute as genuine Prussian blue of good quality :

COMPOSITION OF EIGHT SAMPLES OF COMMERCIAL “PURE” PRUSSIAN BLUE.

	I.	II.	III.	IV.	V.	VI.	VII.	VIII.
Moisture (lost at 100° C.)	5.61	3.54	5.36	5.45	74.53	5.32	5.56	5.61
Water of combination, etc.	15.46	18.18	6.22	13.07	3.08	7.86	14.60	16.93
* Cyanogen	37.72	41.10	42.97	37.90	10.64	39.91	40.19	40.86
† Iron	29.48	32.16	34.27	30.32	7.97	30.94	31.94	31.25
Aluminium	1.82	.52	—	3.17	.72	1.00	1.43	1.52
Alkali metal (Na)	7.60	(K) 4.50	(K) 7.72	(K) 2.25	(K) 1.06	(K) 11.31	(Na) 2.52	.76
Alkaline sulphate	2.31	—	3.46	7.84	2.00	3.66	3.76	(Na) 3.07
	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
* Nitrogen	20.31	22.13	23.14	20.18	5.73	21.49	21.64	22.00
† “Extra radicle” iron	16.66	18.99	19.05	16.04	—	16.21	18.98	19.38

COMPOSITION OF DRY MATTER OF ABOVE SAMPLES (DRIED AT 100° C.).

	I.	II.	III.	IV.	V.	VI.	VII.	VIII.
Water of combination, etc. .	16.38	18.85	6.58	13.87	12.03	8.35	15.46	17.95
* Cyanogen	39.96	42.61	45.41	40.06	41.77	42.14	42.55	43.29
† Iron	31.23	33.34	36.21	32.05	31.30	32.67	33.82	33.09
Aluminium	1.92	.54	—	3.35	2.90	1.03	1.52	1.61
Alkali metal	8.05	4.66	8.16	2.38	4.16	11.94	2.67	0.81
Alkaline sulphate	2.45	—	3.64	8.29	7.84	3.87	3.98	3.25
	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
* Nitrogen	21.52	22.94	24.45	21.57	22.49	22.69	22.91	23.30
† “Extra radicle” iron	17.65	19.69	20.02	16.95	—	17.12	20.09	20.51
Intra-radicle iron (found)	13.58	13.65	16.19	15.10	—	15.55	13.73	12.78
Intra-radicle iron (calculated from nitrogen)	14.34	15.30	16.30	14.38	14.99	15.12	15.28	15.54

In looking at these figures, it will be seen that the percentages of iron and nitrogen do not vary greatly. The amounts of iron in the iron-cyanogen radicle, calculated from the percentage of nitrogen and from the difference between total and extra radicle iron, do not agree closely in all cases. We can offer no explanation of this. Taking the figures for the dry matter, the greatest difference in iron was in the cases of III. and I., 4.98 per cent., and the greatest difference in nitrogen—between III. and I. again—2.93—differences which, calculated on the mean percentages, are under 16 and under 13 per cent. of the totals respectively.

It will also be noticed that seven out of the eight samples contained aluminium. This is not to be considered as an adulterant, as alum is often added to the sulphate

of iron used in precipitating the ferrocyanide without any idea of adulteration, but probably to cause the precipitate to settle better and to dry in a more coherent manner. It probably exists as aluminium ferrocyanide, a compound described by Tissier (*Comp. rend.*, xlv., 232). This has no colouring properties, and, of course, the iron and nitrogen in the iron cyanogen radicle of this compound appear in the total iron and nitrogen as determined. If merely the *ammonia precipitate* is taken and called "ferric oxide," the alumina is included as oxide of iron.

We think that the addition of alum to the precipitating tank is unnecessary, especially as the best sample of blue we have examined contained none.

Alkali metal, as iron-alkali-cyanide, is present in every case. This agrees with the statement of Williamson and others that a blue cannot be obtained free from alkali-metal, except when hydroferrocyanic acid is substituted for alkaline ferrocyanide in the manufacture (the alkaline sulphate present in each case is, of course, due to imperfect washing).

In fact, Prussian blue, if by that term we mean ferric ferrocyanide $\text{Fe}(\text{CN})_{18}$, is not known to the commercial world. Commercial Prussian blue is a mixture of Williamson's blue with other iron-alkali cyanides, and often with aluminium-iron cyanides, altogether a most complex substance.

An examination of the watery extract showed, in the cases of I. and VI., the presence of alkaline ferrocyanide. This is rather remarkable, as with the quantities usually taken the iron is in excess. We believe that these came from the same maker, but are sure, however, that both samples were sent out as bona-fide Prussian blue.

The following notes on appearance of samples in lump and in powder, depth of colour, etc., may be of interest:

Condition.	Appearance.	Powdered Samples.	
		Classification in order of Depth of Colour.	Quality of Tint.
I. Lumps, conchoidal fracture ...	blackish copper glance, but not a bright sheen	2	6
II. Lumps	blue, pale-looking, no coppery glance	6	4
III. Lumps, conchoidal fracture ...	rich blue, bright coppery sheen ...	4	1
IV. Lumps, conchoidal fracture ...	ditto, but not as good as III. ...	3	2
V. Paste	dried, with coppery lustre	—	—
VI. Lumps, conchoidal fracture ...	blackish coppery glance, but not a bright sheen	1	7
VII. Powder	—	7	5
VIII. Lumps	light blue, no coppery glance ...	5	3

The mean percentage of iron in the dry matter of these eight samples was 32.96. This would give 3.03 as the factor for calculating iron to Prussian blue. The mean

percentage of nitrogen was 22.73; this would give as a factor for calculating nitrogen to Prussian blue 4.4. The following tables show the accuracy to which these factors gave the percentage of Prussian blue in the eight samples examined:

In Dry Matter.	I.	II.	III.	IV.	V.	VI.	VII.	VIII.
N $\times$ 4.4	94.69	100.93	107.58	94.91	98.95	99.83	100.80	102.52
Fe $\times$ 3.03	94.63	101.02	109.71	97.11	94.84	98.99	102.47	100.26

Of course, these are merely empirical factors, based on the examination of commercial samples of varying composition, and do not possess the accuracy of a factor to reduce one definite chemical compound to terms of another, but, at any rate, taken together they are of sufficient accuracy for calculating the percentage of Prussian blue in pigments containing that colour. The nitrogen alone in most cases would be sufficient.

We feel justified in stating that blue sold as Prussian blue should contain at least 20 per cent. of nitrogen and 30 per cent. of iron calculated on the dry matter, and, after burning, should be entirely dissolved by hydrochloric acid. A "dry" blue should certainly contain under 7 per cent. moisture. Another important point is that the sulphuric acid used in the Kjeldahl nitrogen determination should not be blackened. Pure cyanides dissolve in sulphuric acid without any charring, which, if it occurs, indicates the presence of organic adulterants. A case of this kind will be noted later.

The watery extract should not indicate the presence of excess of alkaline ferrocyanide. We consider that this is evidence of defective manufacture, although it cannot, of course, be regarded as adulteration. Still it—containing as it does iron and nitrogen—is partly included in the analysis as Prussian blue, whereas it has no pigmentary value, and its solubility in water does not add to the weathering qualities of the colour.

COMMERCIAL PIGMENTS.

The following cases of examination of an adulterated sample of Prussian blue (of German manufacture) and of some colours ground in oil possess some interest.

A rather pale-looking sample of dry powdered Prussian blue, which we were told was a cheap sample of German manufacture, gave only 14.35 per cent. of nitrogen. This at once aroused our suspicions, especially as, instead of becoming colourless in a few minutes on boiling with sulphuric acid, a decided blackening occurred. This clearly pointed to the presence of an organic adulterant. On further examination, the following figures were obtained:

Moisture	11.35
Water of combination, organic adulterant, alkalies, etc.	37.76
Cyanogen*	26.65
Iron	22.67
Aluminium	1.14
Insoluble	.43
	<hr/>
	100.00
Per cent. nitrogen $\times$ 4.4	63.10
„ iron $\times$ 3.03	68.69
* Nitrogen	14.35

This sample not only contained more water than is usual, but was clearly deficient in blue. We think that one is justified in stating that it did not contain more than 70 per cent. of Prussian blue.

Two samples of Brunswick green ground in oil were examined. Brunswick green is a Prussian blue-lead chromate green mixed with barium sulphate ("barytes"). A portion from which the oil had been extracted was gently ignited and treated with hydrochloric acid, the solution of lead, iron, and chromium chlorides filtered from the barium sulphate, and the lead precipitated with sulphuric acid. In the filtrate from the lead sulphate the "ammonia precipitate" containing the mixed oxides of iron and chromium was determined, the oxides were separated by fusion with alkaline carbonate and nitrate and extraction of the fused mass with water, Fe_2O_3 being insoluble. Direct titration with $\text{K}_2\text{Cr}_2\text{O}_7$ was difficult, as the colour of the chromium masked the reduction of the iron with stannous chloride:

	Light-green.	Dark-green.
Oil	11.27	13.55
Prussian blue ($\text{Fe} \times 3.03$)	1.01	4.21
Chrome yellow	4.98	7.10
Barium sulphate	82.74	75.14
	<hr/> 100.00	<hr/> 100.00

The nitrogen was determined in each of these samples in about 5 grammes, and was .19 and .72 respectively, which, using 4.4 as a multiplier, would give .83 and 3.16 per cent. of Prussian blue in these samples. We are much more inclined to rely on a direct determination of this kind than on the determination of the iron by the method described. The method of analysis for these colours described by Hurst, and due to Brown (*Chem. News*, December 31, 1886), seems still more unsatisfactory. The green is treated with hydrochloric acid to dissolve out the lead chromate (of course, as lead and chromium chlorides). The residue, barytes and Prussian blue, is ignited to decompose the blue, weighed, treated with aqua regia to dissolve out oxide of iron (*and alkalies*), and the insoluble portion again weighed. The difference is to be taken as oxide of iron and multiplied by 2.212 to give Prussian blue. The lead and chromium are, of course, determined in the original filtrate.

In the case of colours ground in oil, the Kjeldahl method is particularly applicable for the determination of nitrogen, and, as now it is very general to sell these colours in oil instead of dry, we think that the nitrogen determination will be found a very convenient method of ascertaining (approximately) the amount of Prussian blue in the many diluted colours made from it. Adulteration with nitrogenous matter is not probable, and so is not likely to lead to erroneous results. We intend to continue the examination of all samples which come under our notice by this method, which is rapid (we have obtained a result in under one hour), and at once points to any serious sophistication.

In conclusion, we have to mention that this work was done in the laboratory of the London County Council in the course of our regular official duties. We also desire to express our thanks to Messrs. S. Lambert and Co., Sir William Rose and Co., and Messrs. Colthurst and Harding, for providing us with samples and information respecting their manufacture.