Steam Aniline Black

By Professor *N. Wosnessensky*

I. *Introduction*

Aniline black is one of the most beautiful and stablest of colours and can truly be called the best and fastest black of all. It is very widely used for dyeing and for calico printing owing to the simple and cheap dyeing process, and on account of its important properties, such as beauty of shade and fastness.

Unfortunately the process is to a certain extent poisonous so that this method of working ought, as a matter of fact, to be forbidden, The use of aniline in dyeing and calico printing ought, as a matter of fact, to be forbidden, just as work with arsenic compounds is forbidden. But this cheap and most stable colour is irreplaceable at the present stage of dyestuff chemistry, and textile chemists and hygienists must accordingly try in every way to lessen the danger which is inherent in the use of aniline oil in the textile industry.

This problem can be solved in two directions. Firstly, either the equipment of the workroom must be changed, or, secondly, the quantity of aniline required in the dyeing methods must be reduced. The latter possibility will be here considered.

II. Literature

Before we make any attempt to change any processes, it will be advisable to consider what has been written upon the subject. In this connection the following authors should be mentioned:

1. Noelting, Anilinschwarz, 2nd ed, 1904.
2. Knecht-Fothergill, Textile Printing, 2nd edition.
3. Ullmann, Encyclopädie der technischen Chemie.
4. Heermann, Technologie der Textilveredlung.
5. Axmacher, Führer durch den Zeugdruck.
6. Lauber, Handbuch des Zeugdrucks.
7. Braß, Praktikum der Färberei und Druckerei.
8. Gnehm-Muralt, Taschenbuch der Färberei und Druckerei.
9. Depierre, Traité de l'impression.
10. Farbwerke Höchst, Ratgeber.

The following tabular survey gives a summary of the processes given in these sources.

This table was prepared as follows. In order to secure comparable figures, we have calculated them afresh and reduced them to 1 kilo printing colour (columns 5, 6, 7, 8, 9). Then the total quantity of aniline used was worked out (columns 10, 11), and the corresponding quantities of oxidizing agents (column 3) and K_4FeCN_6 calculated and expressed in percentages of aniline[1]).

The average figure for aniline — 78 grams — is much too high, but such an excess of aniline can be explained by the further discussion of the question. According to these statements about one half of the aniline used is lost in the air, and this fact is confirmed by our being able to produce a good black with 40 grams of aniline per kilo printing paste.

The tabular statement shows that there is not much agreement among the various authorities, so that there remains to be decided which method is correct.

Our investigations will cover three points, corresponding to the three constituents of aniline black.

A. We must first of all determine how far the aniline salts can sublime and decide the question whether the presence of free aniline in the colour is necessary.

B. We must further determine just what part potassium ferrocyanide plays and fix the quantity required accordingly.

C. Finally the quantity of oxidizing agent must be determined that is required to oxidize the aniline used, so as to prevent any loss of it if sufficient oxidizing agent is not present.

A. M. Tschilikin was the first to point out in the literature that free aniline is to be found in the dye liquor which partly evaporates off during drying. The same applies to the printing colour and it can be said in advance that the whole of the aniline in the colour should be neutralized.

According to M. Tschilikin (cf. "Nachrichten") [2]) the quantity of aniline recovered amounts to from 8—12 per cent., but we must recover 50% of the aniline used.

We have therefore to rely upon the complete neutralization of aniline. The question is now, as it was then, whether the excess of aniline can be avoided.

There are several processes according to which the whole of the aniline is to be neutralized (No. 6, 7, 8, 18), but the authors use an excess of aniline.

III. Calculating the quantity of potassium ferrocyanide

B) The nature of this calculation depends upon the part ascribed to the salt. Many authors look upon it as a catalyst, but this would appear not to be correct. Others agam (Noelting, page 66; Georgiewics, page 268) state that KCl and the corresponding salt of aniline are formed in the solution. It should be observed that this aniline salt was pre-

1) These figures have been calculated by several authors on aniline chlorhydrate, but this is wrong, because several salts of aniline are used. We have accordingly regarded the total content of **aniline** as the main point, which is of great importance for us.

2) Izwesti ya textilnoy Promischlennosti, 1925, Nr. 32, page 24. Melliand Textilberichte, 1927, Nr. 3.

Table 1

		page	percentage calculated on aniline		per kilo printing colour			per kilo printing colour		aniline		
			Na ClO_3	K_4 Fe CN_6	aniline salt	free aniline	total aniline	Na ClO_3	K_4 Fe CN_6	neutral. withHCl	free	
1	Noelting	30	48	80			82	39	66	64	18	$(NH_4)_4FeCN_6$
2	—	52	58	49			83	49	41	75	8	aniline ferrocyanide
3	—	52	53	59			85	45	50	76	9	
4	—	75	50	55			70	35	38	53	17	(on tannin ground)
5	—	64	40	43			82	33	36	63	19	
6	—	112	52	90	133		96	50	87	96	0	on wool (26 tartaric acid)
7	—	113	55	69	132		95	50	66	95	0	on wool
8	Knecht	305	46	101	84		60	28	61	60	0	
9	Ullmann IV	159	41	68	95	5	73	30	50	68	5	
10	Heermann	343	40	35	45	55	87	35	30	32	55	55 p. thousand lactic acid
11	—	492	41	68	99	9	80	33	55	71	9	
12	Axmacher	187	53	59			85	45	50			42 K_3 Fe CN_6
13	Lauber	399	57	(74)			56	29	42	38	18	33 $KClO_3$ 7 tartaric acid
14	—	399	47	86	82	14	72	34	62	59	14	44 acetic acid
15	Brass	72	34	68	95	5	73	25	50	68	5	
16	Gnehm	73	63	71	85	5	63	40	45	58	5	
17	Depierre I	425	40	6	104	35	113	45	7	78	35	
18	— III	129	73	108	71		51	38	55	51	0	
19	Farbwerke	288	34	68	94	5	72	25	50	67	5	
20	German Patent 275,845		40	35	45	55	87	35	30	32	55	55 p. thousand formic acid
			48	65			78					

pared by itself according to earlier processes (Noelting, page 52).

In the latter case an equivalent quantity of K_4FeCN_6 must be taken, that is to say, an amount must be taken equal to 113.6% of the quantity of aniline used. The goods are thereby protected from being attacked by the hydrochloric acid set free, because it is neutralized quantitatively to KCl.

IV. Calculation of the necessary quantity of oxidizing agent

C) It is advisable, in order to make use of the whole quantity of aniline taken, to oxidize it as quickly as possible, so that it cannot sublimate off the fabric again.

We are even of the opinion that if working is done properly with following oxidation (e. g. by treating the goods with bichromate) it cannot be calculated at all. The unoxidized aniline adhering to the goods would have partially evaporated in the course of the various treatments to which the fabric is subjected and would therefore be lost. Accordingly it is advisable to conclude that the formula of the quadruple quinoid hydrolized aniline of Willstätter (Berichte 42—44) is correct.

During the transformation from aniline to the substance mentioned 8 molecules of aniline lose 25 atoms of hydrogen, that is to say, we must use $\frac{12.5}{3}$ molecules of potassium chlorate, that is, 59.5% of the weight of the aniline.

Willstätter himself points out (Berichte 42—4128) that 61% chlorate salt are required for the preparation of the quadruple quinoid aniline (he himself used the potassium salt and worked with vanadium). He probably convinced himself that part of the oxygen is lost, and the theoretical figure given above can be regarded as a minimum.

In oxidizing K_4FeCN_6 to K_3FeCN_6 a certain

amount of oxidizing agent is consumed, amounting to about 5% of the weight of aniline.

In this way the total quantity of oxidizing agent is 64% sodium chlorate calculated on the weight of the aniline.

V. Normal process

When the tabulation given above is examined, it will be found that none of the processes given satisfy the conditions just mentioned, but it should be mentioned that process No. 18, according to which the quantity of chlorate even exceeds the theoretical amount, gives the minimum quantity of aniline (reckoned on 1 kilo colour). The other processes deviate even more from the theoretical figures and consequently give larger quantities of aniline. Process No. 17 is of special interest, because it calls for the smallest amount of K_4FeCN_6 and thus yields the largest quantity of aniline.

Upon looking through the various processes which have been reported in the literature of the past fifty years and more it can be seen that their authors have not followed any general leading idea.

VI. Experimental investigation

It is known from the literature that the aniline salts (in particular the aniline salts of organic acids) sublimate and their volatility has several times been determined.

Nowhere, however, is there any reference to the volatility of aniline ferrocyanide. If we accept the formation of this salt, its volatility is of great importance for us.

This investigation is conducted by diazotizing the aniline in combination whith sulphuric acid, which is best done by using 4 molecules H_2SO_4 to 1 molecule aniline. The results are shown in the following table which gives the percentage figures directly.

	Aniline content before drying	after drying at 60°C on the fabrik	after drying at 60°C in the solvent	Loss
Chlorhydrate .	100%	82,3	15.7	2
Tartrate	100%	93,9	4.31	1.79
Ferrocyanide . .	100%	80	9.21	10.79

The small loss shown in the first two analyses indicates that they were comparatively exact. The excessive loss in the third case is striking, but it can easily by explained. The third test on white fabric impregnated with the aniline salt dyed greyish brown in contrast to the other two. It is thus proved that part of the aniline was oxidized and was lost for the analysis.

The latter observation permits us to explain the part played by potassium ferrocyanide: the aniline ferrocyanide can be oxidized even in the air.

VII. Working process

The calculations quoted above give us the practical application. There were taken 40 grams aniline (figured on 1 kilo colour), 45 grams K_4FeCN_6 (100% of the theoretical), 26 grams, later 28 grams, chlorate (that is, 60—70%; rather more than theoretically required).

It was thereby found that the shade of aniline black becomes reddish in the strong oxidation and that the aniline is not completely used up when the oxidation is insufficient, as can better be seen when letting down the colour.

The use of tartaric acid makes the shade greener. (The salts formed are potassium tartrate and the corresponding salt of aniline. The fine crystals of the precipitate which mix with the printing colour do not cause the slightest trouble.) The result was good and the goods were first printed according to the following recipe:

40 aniline
40 HCl 19° Bé
822 thickening and water
50 K_4FeCN_6
20 tartaric acid
26 sodium chlorate

made up to 1000.

Then the amount of potassium ferrocyanide was reduced to 40 grams without having much effect upon the strength of the fabric.

In one mill thousands of pieces were printed in this way and in many others test runs were made.

It is further evident that good results are obtained without tartaric acid if the whole of the aniline oil is carefully neutralized. If tartaric acid is not used, the more delicate parts of the pattern appear rather reddish, which is particularly noticeable when the prints are made with only 30 grams aniline per kilo (that is to say when let down 3/1). On the whole, however, the results are quite satisfactory. The strength of the goods is better than formerly when free aniline was

used, losing, as they do, only from 8—10% in strength. After the prints have been steamed for a short time, they can be steamed for one hour longer without adding chloride of ammonia, after which the strength of the goods is 97%, taking the strength after the short steaming as 100 per cent.

These tests give us the following recipe:

40 aniline oil
— HCl till completely neutralized
— thickening
40 potassium ferrocyanide
26 sodium chlorate

made up to 1000.

Many thousands of pieces were printed with aniline black according to this recipe in the works of the Trechgornaia Manufaktur[3]).

The printing colour suffers no change within one to two days. After that it turns darker, but that causes no trouble.

In regard to health conditions, it is to be recommended to use aniline salt which has been prepared beforehand instead of aniline oil with acid, because aniline salt is less dangerous. The quantity of chlorate depends upon its dryness and upon the conditions in the Mather-Platt ager, and can vary from 60 to 70% of the weight of aniline taken.

In the next article we shall discuss the aniline black padding solutions which are of special interest.

3) Formerly Prochoroff Works.