

# Study of Toning Processes for Photographic Paper

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## Introduction

Toning is a process giving a possibility to change black or grey colour of a print as a result of a transformation of image silver into colored chemical compounds or a dye<sup>1,2</sup>.

Dyeing of photographic image into sepia (different hues of brown from purple brown to yellow brown) is usually made by a transformation of metallic silver into silver sulfide with the use of sodium sulfide, thiourea or other sulfur-containing compounds.

By converting metallic silver into colored metal salts is possible to change a black and white image into many different colors. Thus, toning by salts of iron gives the image dyed in blue, by salts of uranium - in red brown, by salts of copper - from pink orange to dark cherry, by salts of nickel - in bright red, by salts of lead - in yellow. To obtain some colours and their hues several salts of different metals are used simultaneously, e.g. to obtain green salts of iron and lead are used.

## Experimental and Discussion

Two types of developers were used:

"a", compensating developer Kodak D-76 giving saturated black tones;

"b", a developer giving warmer (brown) tones, with the following composition: Na<sub>2</sub>SO<sub>3</sub> 38 g, hydroquinone 10 g, K<sub>2</sub>CO<sub>3</sub> 50 g, KBr 1 g, H<sub>2</sub>O up 1 l.

However, these tones differ only while comparing samples. We can speak only about slight hues of colours. That's why we generally used developer D-76. The cases when the initial samples were developed by the "b" developer are specially marked.

Three types of photographic paper were chosen for investigation (the sample's numbers are marked by numerals)

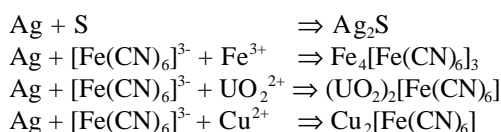
1 - "AGFA" MCC118FB, multicontrast, classic, fine grained matt;

2 - "Ilford" IV RC Deluxe mgd.1M, multigrade, resin-coated base;

3 - "Samshite" (produced by "Slavich" TU 6-56-00205133-30-92, Pereslavl, Russia) white, normal contrast, medium weight, resin-coated base.

## Direct Toning

The scheme of chemistry of direct toning process:



For direct toning we used the following toning solutions:

<b>DT1</b>		
Na <sub>2</sub> S·9H <sub>2</sub> O		0,1M
<b>DT2</b>		
Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> ·5H <sub>2</sub> O		0,1M
H <sub>2</sub> SO <sub>4</sub>		0,1M
<b>DT3</b>		
"1" - K <sub>3</sub> [Fe(CN) <sub>6</sub> ]	0,05M	
"2" - FeCl <sub>3</sub> ·6H <sub>2</sub> O		0,05M
Working solution "1"+"2"=1+1		
<b>DT4</b>		
"1" - K <sub>3</sub> [Fe(CN) <sub>6</sub> ]	0,05M	
"2" - CuSO <sub>4</sub> ·5H <sub>2</sub> O		0,05M
Potassium citrate		0,2M
Working solution "1"+"2"=1+1		
<b>DT5</b>		
"1" - K <sub>3</sub> [Fe(CN) <sub>6</sub> ]	0,05M	
K <sub>2</sub> CO <sub>3</sub>		0,05M
"2" - CuSO <sub>4</sub> ·5H <sub>2</sub> O		0,05M
(NH <sub>4</sub> ) <sub>2</sub> C <sub>2</sub> O <sub>4</sub>		0,2M
Working solution "1"+"2"=1+1		

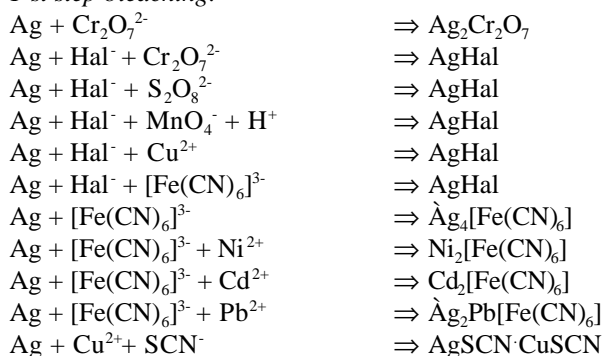
**Table 1**

Samples number	Toning solution	Photo-paper	Colour
1	control sample	1	Black
2	control sample	2	Black
3	control sample	3	Black
4	DT1 (t = 60 °C)	3	Black-brown
5	DT2 (t =45-60 °C)	1	Dark-brown
6	DT2 (t =45-60 °C)	3	Brown
7	DT3	3	Blue
8	DT3 followed by DT1	3	Olive-brown
9	DT4	1	Dark-red-brown
10	DT4	3	Red-brown
11	DT4 followed by DT1	3	Olive-brown
12	DT5	1	Dark-violet-red
13	DT5	3	Violet-red
14	DT5 followed by DT1	3	Dark-olive-brown
15	DT5 followed by 25% NH <sub>3</sub> aq	3	Sepia

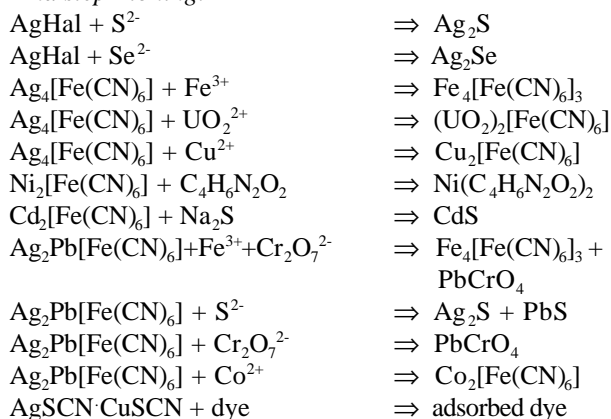
**Indirect Toning**

The scheme of chemistry of indirect toning process:

*1-st step-bleaching:*



*2-nd step - toning:*



For indirect toning we used followed bleach solutions:

<b>B1</b>		
K <sub>3</sub> [Fe(CN) <sub>6</sub> ]		0,1M
<b>B2</b>		
K <sub>3</sub> [Fe(CN) <sub>6</sub> ]		0,1M
Na <sub>2</sub> CO <sub>3</sub>		0,2M
a - KCl		0,1M
b - KBr		0,1M
c - KI		0,1M
<b>B3</b>		
K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub>		0,1M
H <sub>2</sub> SO <sub>4</sub>		0,1M
a - KCl		0,1M
b - KBr		0,1M
c - KI		0,1M
<b>B4</b>		
"1" - KMnO <sub>4</sub>		0,03M
a - KCl		0,1M
b - KBr		0,1M
c - KI		0,1M
"2" - H <sub>2</sub> SO <sub>4</sub>		0,1M
"3" - K <sub>2</sub> S <sub>2</sub> O <sub>5</sub>		0,1M
Working solution: "1" + "2" = 1+1.		
Colourless in solution "3".		
<b>B5</b>		
(NH <sub>4</sub> ) <sub>2</sub> S <sub>2</sub> O <sub>8</sub>		0,1M
H <sub>2</sub> SO <sub>4</sub>		0,1M
a - KCl		0,1M
b - KBr		0,1M
c - KI		0,1M
<b>B6</b>		
K <sub>3</sub> [Fe(CN) <sub>6</sub> ]		0,1M
Pb(NO <sub>3</sub> ) <sub>2</sub>		0,05M
CH <sub>3</sub> COOH		0,5M
<b>B7</b>		
"1" - CdCl <sub>2</sub>		0,2M
"2" - K <sub>3</sub> [Fe(CN) <sub>6</sub> ]	0,1M	
"3" - Potassium citrate		1M
Working solution: "1" + "2" + "3" = 1+1+1.		
<b>B8</b>		
"1" - Potassium citrate		1M
"2" - NiCl <sub>2</sub> ·6H <sub>2</sub> O		0,1M
"3" - K <sub>3</sub> [Fe(CN) <sub>6</sub> ]	0,1M	
Working solution: "1" + "2" + "3" = 1+1+1.		
<b>B9</b>		
CuSO <sub>4</sub> ·5H <sub>2</sub> O		0,5M
H <sub>2</sub> SO <sub>4</sub>		0,1M

- a - KCl 0,1M
- b - KBr 0,1M
- c - KI 0,1M

For indirect toning we used followed solutions:

- T1**  
C<sub>4</sub>H<sub>6</sub>N<sub>2</sub>O<sub>2</sub> 0,1M  
NaOH 0,4M
- T2**  
CuSO<sub>4</sub>·5H<sub>2</sub>O 0,2M  
HNO<sub>3</sub> 0,1M
- T3**  
FeCl<sub>3</sub>·6H<sub>2</sub>O 0,1M
- T4**  
CoCl<sub>2</sub>·6H<sub>2</sub>O 1M
- T5**  
FeCl<sub>3</sub>·6H<sub>2</sub>O 0,1M  
K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> 0,02M
- T6**  
K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> 0,1M
- T7**  
Na<sub>2</sub>S·9H<sub>2</sub>O 0,3M

**Table 2**

Samples number	Bleach	Toning solution	Photo-paper	Colour
16	B1	T3	1*	Dark-blue
17	B1	T3	1	Blue
18	B1	T3	2	Blue
19	B1	T3	3	Light-blue
20	B1	T2	1*	Brown
21	B1	T2	1	Brown
22	B1	T2	2	Beige
23	B1	T2	3	Light-brown
24	B1	T2 followed by T7	1*	Black-brown
25	B1	T2 followed by T7	2	Black
26	B1	T2 followed by T7	3	Dark-brown-red
27	B1	T7	1*	Brown
28	B1	T7	2	Black
29	B1	T7	3	Light-olive-brown

30	B1	T4	1	Green
31	B1	T4	3	Light-green
32	B2a	T3	1	Dark-blue
33	B2a	T3	1*	Blue
34	B2a	T3	2	Dark-blue
35	B2b	T3	2	Grey
36	B2c	T3	2	Light-yellow
37	B2a	T3	3	Blue
38	B2b	T3	3	Grey
39	B2a	T2	1*	Brown
40	B2a	T2	1	Beige
41	B2a	T2	2	Beige
42	B2b	T2	2	Grey
43	B2c	T2	2	Light-yellow
44	B2a	T2	3	Beige-red
45	B2b	T2	3	Grey
46	B2c	T2	3	Light-yellow
47	B2a	T7	1	Dark-brown
48	B2a	T7	2	Black-brown
49	B2b	T7	1	Dark-brown
50	B2b	T7	2	Black-brown
51	B2c	T7	1	Brown
52	B2c	T7	2	Black-brown
53	B2c	T7	3	Light-brown
54	B6	T2	3	Violet-red
55	B6	T3	3	Blue
56	B6	T3 followed by dev."b"	3	Olive
57	B6	T4	3	Green
58	B6	T4 followed by NH <sub>3</sub> aq	3	Light-brown
59	B6	T6	3	Yellow
60	B6	T6 followed by dev."b"	3	Yellow-brown
61	B6	T5	3	Dark-green
62	B6	T5 followed by NH <sub>3</sub> aq	3	Dark-yellow-brown
63	B7	T7	1	Light-yellow
64	B8	T7	2	Dark-brown
65	B8	T1	1	Purple (high fog)
66	B8	T1	2	Light-brown-purple
67	B8	T1	3	Purple
68	B8	T1 followed by T4	3	Violet-purple

69	B8	T1 followed by T4, T7	3	Brown-purple
70	B8	T1, T4, NH <sub>3</sub> aq	3	Light-violet-purple

It is possible to use B3, B4, B5, B9 bleach instead of B2 bleach in the cases "a", "b", "c".

The experimental results of toning of given samples are given in the tables above.

The colour of image depend on very many factors, the toning chemistry, purity of the chemicals, consistent procedures, homogeneity and size of silver grains, emulsion coating thickness, developing conditions, counterion types, etc.

Preparation for toning. Before toning the prints should be correctly exposed (except in some special case) and developed, well fixed and carefully washed. While washing it is recommended to use hypo clearing agent and controlled washing. While printing and developing it is necessary to use developer giving purely black or neutral grey tones on the prints.

If a high concentration of potassium bromide is used in the developer, subsequent toning will produce a warmer tonality.

As a general rule if toning is achieved by the use of sulfur compounds the density of the toned image decreases, if use is made of metal salts, density increases in the toned image. The use of copper, lead or uranium compounds, produces images whose colors change gradually (according to a definite sequence) as the toning proceeds. In toning processes that use sulfur compounds, toning should be carried out to completion, which is indicated by a stable image color.

### References

1. V.P.Mikulín, Handbook of photographic recipes, 3rd edition (1969).
2. V.A.Yashtold-Govorko, Photoexposure and photodevelopment, 3rd edition (1967).

### Acknowledgment

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