Paper B23

Study on Dyeing Technology of Chrome-free Leather and Fur

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Abstract: Nowadays, the chrome-free tanning process had become the focus of leather industry, but the research about dyeing technology for chrome-free leather is not good enough. The dyeing processes on three kinds of chrome-free leather and one kind of fur have been studied in this paper, such as P-Al combination tanned fur dyeing by using Fur red F-SY and Fur blue F-TB, vegetable tanned leather by using Cationic brilliant red and Basic rhodamine, modified glutaraldehyde tanned leather by using basic Rhodamine, and phosphine tanned leather by using a variety of acid dyestuffs including AF135, BSF RL, BSF N3G, NGS, etc. And the control confirmatory dyeing experiments of acid black ATT with basic dyestuffs including Basic blue, Basic rhodamine, Basic peach red, Basic black were did to make analysis. The dyeing optimum condition was determined by measuring dye uptake rate, penetration, the leveling and the shade of dyeing of them separately under different conditions, such as pH, temperature, time, dyestuff fixing parameter and so on.

The results show that: 1. the basic dyestuffs performs well on those three kinds of chrome-free leather than acid dyeing. Aside from acid black ATT, the dyeing results of other acid dyestuffs were all imperfect, and the penetrations were worse and hardly dyed through the cross-section of leather. 2. The starting pH of dyeing for chrome-free leather were different from chrome tanned leather, the dyeing should be proceeded at pH3.3~3.8 at the beginning. The leather tanned with different chrome-free tanning agents had different optimal pH, but it was good to raise pH with proper alkali for raising dye up-taking rate and color fixing in later period. 3. Dyeing of vegetable tanned leather should be proceeded at pH3.3~3.8 decreased by adding acid for 60min and then raised pH to around 4.50 gradually for 30min~40min that dye up-taking rate could reach 98%; Modified glutaraldehyde tanned leather should be neutralized for 60 min at normal temperature, then added in assistant (such as salt), adjusted pH to around 3.5, dyeing for 40 min~50 min, and raised pH to around 4.0 to fix dyestuff. The pH of phosphine tanned leather should be decreased to 4.0~4.5, dyeing for 60 min, then gradually elevating pH to 6.5 to fixing dyestuff by adding alkali for 30~40 min .The dye up-taking rate could be further improved by adding in anionic retanning agent to fix dyestuff for 10~20 min after dyeing. 4. The dyeing temperature of chrome-free leather should be controlled at 40ºC and the dosage of dyestuff should be 2% with float 2. 5. The conditions of fur dyeing taken in this experiment is appropriate which is good for penetration, fixation, uniformity and promoting dye up-taking rate.

Keywords: chrome-free tanning; dyeing; vegetable tanned leather; modified glutaraldehyde tanned leather; phosphine tanned leather; P-Al combination tanned fur.

1. Introduction

The tanning agent which ranks foremost today is chrome tanning agent for its fantastic comprehensive performance compared with mineral tanning agent, syntans, vegetable tanning agent and so on[1]. But the production process will cause serious environmental problems which are harmful to human and animals[2] that tanning industry gradually focuses on how to produce ecological leather by the use of clean and ecological chrome-free tanning agent. The research shows that vegetable tanning agent is biodegradable product of nature[3], and the production of modified glutaraldehyde tanned leather and phosphine tanned leather are also cleaner than chrome tanned leather, the reason why they fail to become mainstream product in the market is the single color and monotonous style of finished leather. The appearance of leather can be improved through dyeing keeping pace with popular style, satisfying fashion requirements of people, adapting to the needs of variable uses, and increasing the value of commodities[4], therefore, how to enrich diversity of chrome-free tanned leather through dyeing is especially significant. The dyeing process parameter of chrome free tanned leather was determined on the basis of contrastive study on dyeing performance of basic and acid dyestuff and discussing the effect of dyeing condition on dyeing performance.

2. Materials and Methods

2.1 materials and instruments

Materials and instruments used in this experiment are shown in table 1 and table 2 .

Table 1. materials

Source	Category	Material name
BASF corporation	Industrial goods	BSF RL; BSF N3G
Chengdu KeLong Chemical Agent factory	AR	Acetic acid(36%); Anhydrous sodium sulfate; Sod. bicarbonate
Tianjin revitalization chemical plant	Industrial goods	Basic rhodamine; Peregal (Nonionic penetrating agent)
Beijing FanBo Sci. & Tech. Corporation	Industrial goods	Fur blue F-TB; Fur red F-SY
Clariant Corporation	Industrial goods	AF 135; Granofin FCC
Zhe Jiang Runtu Corporation	Industrial goods	Cationic brilliant red
Taiwan Yongguang Chemical Corporation	Industrial goods	EVERLAN BLACK NGS
The Third Plant of Tianjin Chemical Dyes	Industrial goods	Acid black ATT
Tianjin Jinlonglai chemical Co., Ltd.	Industrial goods	Basic black; Alkali blue
Purchase and Supply Station of Tianjin Chemical Factory	Industrial goods	Safranine

Table 2. Instruments

Instrument	Source
Du drum(100mm×200mm)	Wuxi Derui Chemical Machinery Co., Ltd.
HZS-H Bath Oscillator	Harbin Donglian Electronic Tech. Development Co., Ltd.
722 Spectrophoto Meter	Shanghai Precision Scientific Instrument Co., Ltd.

2.2 Methods

2.2.1 Dyeing Experiment

Chrome free tanned leather is cut into small pieces(1 cm×10 cm, 2 cm×10 cm,etc.)for contrast test of dyeing after wringing and weighing as the basis of materials used in following test.Comparing the change of dye uptake rate and penetration under different process conditions such as initial pH, temperature(T), time(t), float ratio(F), concentration and the alkali degree by measuring absorbency of dye liquor every 10 minutes and observing penetration circumstance of incision every 20 minutes.The color uniformity and the shade of dyeing are observed after drying[5].

The dyeing of P-Al combination tanned rabbit fur is carried out under a fixed condition applied to actual production. Weighing the fur as the basis of materials used in following test, then determining the dye up-taking rate and the degree of penetration after 90 min. The color uniformity and the shade of dyeing are observed after drying[5].

2.2.2 Leather Making Flow Chart

1. pickling-depickling-vegetable tanning-washing-rinsing-adjusting pH-dyeing-fixing-air drying
2. pickling-depickling-modified glutaraldehyde tanning- adjusting pH-Dyeing-Fixing-air drying
3. Pickling-depickling-phosphine tanning-basifying-washing-adjusting pH-dyeing-fixing-air drying

2.2.3 Determination of dye up-take rate

Determining according to method in document [5 ,6].

3. Results and discussion

3.1 Results and discussion of vegetable tanned leather

3.1.1 Effect of pH on the dyeing performance

Vegetable tanned leather was adjusted to different pH by dealing with acetic acid or sodium bicarbonate for 60 minutes before dyeing, and also adjusted the pH of dyeing liquor to the same value as leather, then dyed. Other dyeing conditions: T=40ºC, dosage=2%, F=2, t=60min. The dyeing results are shown in table 3 and table 4.

Table 3 and table 4 show that dye up-taking rate of cationic brilliant red and basic rhodamine has a tendency of elevation, the color shade becomes deeper, and the color uniformity get worse along with pH elevation at 10 minutes. So low pH is conducive to penetration of dyestuff. This is because basic dyestuff is positively charged and the isoelectric point of vegetable tanned leather is 3.2~4.0[7]. Vegetable tanned leather is negative charged above the isoelectric point. If anionic dyes(acid dyes or direct dyes)are used for dyeing ,the leather can't be fully shaded[5] and it will be difficult for dyes to fix on the leather surface because of the exclusion between like charges. However, cationic dyes(basic dyes)are positive charged which have a great affinity to it. The carboxyl group is closed when below the isoelectric point, and the mutual exclusive between like charges slows down the speed of fixation of dyestuff with leather whereas is advantageous to penetration.

It's determined that initial pH 3.3~3.8 is the best value in this experiment by comprehensively considerated with penetration ,final dye up-taking rate ,color shade and color uniformity.

Table 3. The dyeing performances of Cationic brilliant red at different pH

No.	pH before dyeing	pH after dyeing	DR at 10 min/%	Final DR/%	S	L	Degree of penetration			
							20 min	40 min	60 min	After drying
1#	2.38	2.73	85.2	92.1	N	G	1/2	2/3	F	F
2#	2.77	3.07	87.7	94.2	N	G	2/5	3/5	F	F
3#	3.01	3.41	88.9	94.9	N	G	1/4	1/3	2/3	3/4
4#	3.32	3.58	92.0	96.5	N	G	2/3	3/4	F	F
5#	3.67	3.87	90.3	96.2	N	G	2/3	F	F	F
6#	3.87	4.05	90.7	96.9	N	G	2/3	3/4	AF	F
7#	4.41	4.42	89.4	97.2	N	G	1/4	1/3	2/5	2/3
8#	4.97	4.89	94.0	99.0	D	G	S	1/4	1/3	1/2
9#	5.52	5.58	93.0	98.6	D	N	S	1/6	1/5	1/4
10#	5.94	6.07	95.9	98.7	D	N	S	1/5	1/4	1/3
11#	6.3	7.03	96.8	97.3	Very D	N	S	S	1/5	2/7

N=Normal, G=Good, S=Shade, F=full, AF=Almost full, D=Deep, DR=Dye uptake rate, L= leveling, S= Surface

Table 4. The dyeing performances of Basic Rhodamine at different pH

No.	pH before dyeing	pH after dyeing	DR at 10 min/%	Final DR/%	S	L	Degree of penetration			
							20 min	40 min	60 min	After drying
1#	2.76	2.95	72.3	95.3	N	G	1/4	1/4	1/3	1/3
2#	2.98	3.16	67.0	94.9	N	G	1/4	1/3	1/3	1/3
3#	3.19	3.32	63.5	97.2	N	G	1/5	1/4	1/3	1/3
4#	3.49	3.59	74.9	99.0	N	G	1/4	1/3	1/3	1/3
5#	3.79	3.79	75.2	97.3	N	G	1/5	1/4	1/4	1/3
6#	4.05	3.96	74.8	98.0	N	G	1/5	1/5	1/4	1/4
7#	4.50	4.33	70.7	96.1	N	G	1/5	1/4	1/4	1/4
8#	4.87	4.66	92.7	98.6	D	N	1/5	1/4	1/4	1/4
9#	5.26	4.51	87.3	94.8	D	N	1/6	1/5	1/5	1/4
10#	5.71	5.7	90.8	95.7	D	N	1/6	1/6	1/5	1/5
11#	6.02	6.09	89.8	95.0	Very D	N	1/7	1/6	1/6	1/6

N=Normal, G=Good, S=Shade, F=full, AF=Almost full, D=Deep, DR=Dye uptake rate, L= leveling, S= Surface

3.1.2 Effect of temperature on the dyeing performance

Studying the effect of temperature on dyeing performance on the basis of determining initial pH=3.3~3.8, the results are shown in table 5.

Table 5. The dyeing performances of Basic dyestuff at different temperature

Dyestuffs	T /℃	DR at 10 min/%	Final DR/ %	S	L	Degree of penetration			
						20/min	40/ min	60/min	After dry
Cationic brilliant red	30	89.0	92.1	N	G	1/3	1/2	1/2	F
	40	88.7	94.2	N	G	1/2	2/3	F	F
	50	87.1	94.9	N	G	1/4	1/3	AF	1/3
Basic rhodamine	30	85.7	96.7	N	G	1/6	1/5	2/7	1/3
	40	78.2	98.7	N	G	1/6	1/5	2/7	1/4
	50	80.6	97.8	N	G	1/6	1/5	1/5	F

N=Normal, G=Good, S=Shade, F=full, AF=Almost full, T=temperature, DR=Dye uptake rate, L= leveling

Table 5 shows that the best penetration of Cationic brilliant red performances at 40ºC for having reached full impregnated at 60 minutes while it's not good enough at 30ºC only with two-thirds penetration after drying. And the highest final dye up-taking is inspected at 30ºC, 40ºC followed. Penetration of Basic rhodamine isn't as good as Cationic brilliant red that even can't be full impregnated after drying. It's relatively good in conditions of 30ºC and 40ºC that can be one-third impregnated. The highest final dye up-taking is inspected at 40ºC, 50ºC followed. Finally, it can be concluded that 40ºC is the optimum dyeing temperature of basic dyestuffs in aspects of penetration, dye up-taking rate and the rate of dyeing compared to other temperatures in this experiment.

3.1.3 Effect of dosage on the dyeing performance

Experimental conditions: pH=3.3~3.8, F=2, T=40ºC. 2% and 3% basic dyestuffs (Cationic brilliant red and Basic rhodamine) are used for dyeing 60 min.

Table 6. The dyeing performances of Cationic brilliant red at different dosage

Dyestuff	Dosage	DR at 10 min/%	Final DR/%	Degree of penetration	Shade	C
Cationic brilliant red	2%	88.8	95.1	Full	Slightly Light	G
	3%	86.6	93.1	3/4	Deep	RG
Basic rhodamine	2%	83.5	98.6	1/4	Slightly Light	G
	3%	59.4	96.5	1/4	Deep	RG

F=full, G=Good, RG=Relatively Good, DR=Dye uptake rate, L= leveling

Comparing the data in table 6, it could be seen that basic dyestuff performances better at the dosage of 2% in terms of penetration, final dye up-taking rate and color uniformity. The shade of leather dyed at 2% is a little light while the other one is deep, this may because the surface of leather combines more dyestuffs at the storage of 3% than 2%.Therefore it can be concluded that the amount of 2% of dyestuffs is more appropriate considering general dyeing effect and economic point of view,

and the dosage can be increased or decreased in practical production according to the need.

3.1.4 Effect of time on the dyeing performance

Experimental conditions: pH=3.3~3.8, F=2, T=40ºC, dosage=2%. Dyeing 100 min and inspecting the degree of penetration and dye up-taking rate every 20 min.

Table 7. The Penetration of Cationic dyeing at different time

Time/min	20	40	60	80	100	After drying
Cationic brilliant red	1/2	2/3	Full	Full	Full	Full
Basic rhodamine	1/6	1/5	1/4	2/7	2/7	1/3

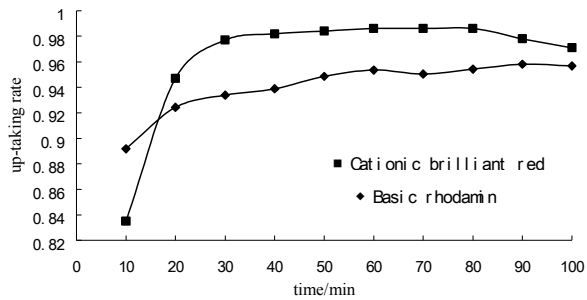

Figure 8. Dye uptake rate VS time

Table 7 and figure 8 show that Cationic brilliant red permeates better than Basic rhodamine and the longer time is taken, the better dyestuffs penetrates. Cationic brilliant red has already completely penetrated while Basic rhodamine just gets degree of one-forth at 60 min, and the degree of penetration has no obvious improvement with extension of time. Simultaneously the dye uptake rate has little change after 40 min and even declines slightly after 70 min. So 60 min is enough when regarding dye uptake rate and degree of penetration as standard without consideration of the fixation, or the total time should be extended to 100 min.

3.1.5 Effect of basification during the later period on the dyeing performance

Table 9 shows that both of the up-taking rate of Cationic brilliant red and Basic rhodamine are improved after dyeing 60 min along with addition of alkali, and the rate reaches maximum value at a certain pH, then the rate decreases along with the promotion of pH. The maximum dye up-taking rate of Cationic brilliant red gets highest at pH 4.67 and 5.14,and the rate of Basic rhodamine reaches it at pH 4.53.

So it can be concluded that it's necessary to raise pH with proper alkali for not only raising dye uptake rate but also promoting the combination between positive charged cationic dyes and negative charged leather because of the attraction between opposite charges in later period. It's determined that the final pH should be controlled around 4.5 and the time of color fixing can be controlled around 30 min~40 min.

Table 9. The dyeing performances of Cationic brilliant red at different degree of basification during the later period of dyeing

dyes	N	Maximum DR/%	Corresponding pH	Time/min									
				0	60		70		80		90		100
				pH BD	DR/%	pH AB	DR/%	pH AB	DR/%	pH AB	DR/%	pH AB	DR/%
Cationic brilliant red	1#	96.1	3.85	3.62	95.4	3.83	95.0	3.85	95.4	3.85	95.8	3.85	95.7
	2#	95.0	4.02	3.57	94.2	3.83	94.3	3.92	94.7	3.97	94.8	4.02	95.0
	3#	95.9	4.51	3.59	94.0	4.19	95.6	4.30	95.0	4.41	95.6	4.51	95.9
	4#	97.7	4.67	3.53	95.9	4.22	96.3	4.47	97.2	4.62	97.6	4.67	97.7
	5#	97.7	5.14	3.56	94.8	4.57	96.0	4.80	97.5	5.14	98.1	5.48	97.9
	6#	96.8	5.87	3.51	95.5	4.84	96.9	5.11	97.3	5.43	98.1	5.87	98.3
Basic rhodamine	1#	96.5	3.31	3.34	92.0	3.32	93.9	3.32	96.9	3.31	96.9	3.30	96.5
	2#	96.8	4.05	3.41	94.0	3.59	95.7	3.65	96.8	3.74	96.8	4.05	96.8
	3#	97.5	4.26	3.40	92.4	3.77	95.9	3.93	97.1	4.07	97.1	4.26	97.5
	4#	98.0	4.33	3.41	92.4	3.94	97.0	4.08	98.0	4.33	98.0	4.77	97.3
	5#	98.2	4.53	3.41	93.4	4.15	98.1	4.53	97.5	4.91	97.5	5.22	97.4

N=number, pH AB=pH after basification, DR=Dye up-taking rate, pH BD=pH before dyeing

3.2 Results and discussion of modified glutaraldehyde tanned leather

3.2.1 Effect of pH on the dyeing performance

Experimental conditions: liquor ratio=2, dosage of dyestuff=2%, temperature=40ºC, time=60 min. The pH of dye bath and crust leather should be kept the same.

Table 10 shows that the highest final dye up taking rate 59.34% is reached by 2# at pH 3.52 and the color uniformity and shade of dyeing are also the best at this pH. In aspect of penetration, all the samples are full impregnated after 20 min, that is to say Basic rhodamine is good at permeating to modified glutaraldehyde tanned leather.

Figure11 shows that the higher the pH is, the faster the crust leather is dyed, but the dye uptake rate decreases unsteadily when the pH is too high.

Isoelectric point of modified glutaraldehyde tanned leather may be 3.50~4.0 gathered from the results above. It's difficult for Basic rhodamine to combine with fiber of crust leather because they have opposite electric charge when pH is lower than isoelectric point. On the contrary, the rate of combination will be much faster if pH is higher than isoelectric point, but the surface of leather would be over dyed which will affect color uniformity and lead to uneven shade and dark color.

So, it can be concluded that the dyeing initial pH should be controlled around 3.5 in this experiment.

3.2.2 Effect of temperature on the dyeing performance

Experimental conditions: F=2; pH=3.5, dosage=2%, t=60 min. Dyeing at 40ºC, 50ºC, 60ºC.

Table 12 and figure 13 show that the dye up-taking rate elevates along with increase of temperature but the color uniformity decreases, and the penetration is very good at any experimental temperature. So, it's appropriate to control temperature around 40ºC, and it's also more in line with the

requirements of actual production from economic point of view.

Table 10. pH on dyeing performance

Number	Dyeing pH	Final dye up-taking rate	Degree of penetration at 20 min	Shade
1#	3.03	48.07%	Full	Relatively uniformity
2#	3.52	59.34%	Full	uniformity
3#	4.00	59.19%	Full	nonuniformity
4#	4.45	46.77%	Full	nonuniformity,local dark

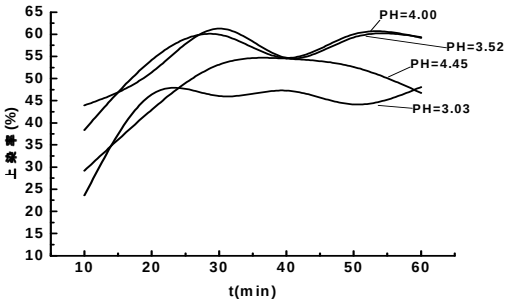

Figure 11 the dye uptake rate under different pH

Table 12. dyeing performance of basic rhodamine dyeing modified glutaraldehyde tanned leather at different temperatures

Temperature/℃	Final dye uptake rate / %	Degree of penetration	
		20 min	After drying
40	59.34%	Full	Good color uniformity and even shade
50	60.21%	Full	uneven color and local dark spots
60	65.07%	Full	Bad color uniformity, dark and coarse surface

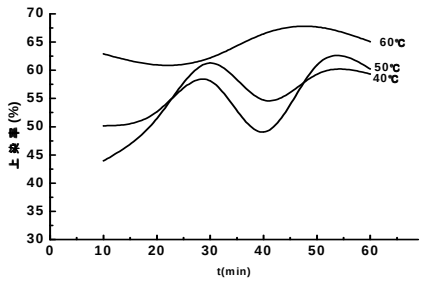

Figure 13. the dye uptake rate of basic rhodamine dyeing modified glutaraldehyde tanned leather at different temperatures

3.2.3 Effect of basification during the later period on the dyeing performance

Experimental conditions: pH of crust leather and dye liquor=3.5, T=40ºC~50ºC, F=2. Basifying the samples every 10 min with sod. bicarbonate solution slowly after dyeing 50 min except for 1# regarded as blank sample and measuring dye up-taking rate and pH of dyeing liquor each time, totally 6 times.

Table 14 and figure 15 show that basification in later period can improve dye up-taking rate and pH 4.00 is appropriate for high pH weakens the function insteadly.

Table 14. the changes of pH at different time

Number	Final dye up-taking rate	0min	50min	60min	70min	80min	90min	100min
		pH						
1#	52.49%	3.52	3.70	3.65	3.68	3.66	3.70	3.74
2#	53.53%	3.53	3.76	3.77	3.83	3.93	4.12	4.40
3#	57.35%	3.53	3.76	3.78	3.90	4.00	4.17	4.70
4#	61.95%	3.51	3.70	3.75	3.88	4.05	4.04	4.04

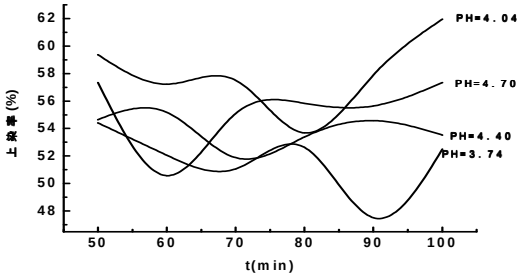

Figure 15. the effect of the dye uptake rate with later basification

3.2.4 Effect of auxiliaries on the dyeing performance

Common additives such as non-ionic Peregal, neutral salt like anhydrous sodium sulfate and salt are added in order to make dyestuff dissolved and dispersed better, and promote the uniformity of penetration and combination of dyes. Mixing additives and dyes by 1:1 to inspect their compatibility firstly. The results are shown in table16.

Table 16 shows that the compatibilities of additives chosen in this experiment and basic rhodamine are all good so that they can be one-bath dyed.

The additives are added in during neutralization process lasting 60 min at the dosage of 2. Dyeing conditions: dosage=2%, F=2, T=40ºC, pH=3.5, t=60min. The results are shown in figure 17.

Table 16. the compatibility of Additives and Basic Rhodamine

Additive	Peregal	Anhydrous sodium sulfate	Salt
Compatibility	Good	Good	Good

Figure 17 shows that: additives used in this experiment have an effect on dye up-taking rate and the salt play a more significant role in promoting the rate of dyeing to a certain extent, but also decreases final dye up-taking rate. Peregal and anhydrous sodium sulfate have a similar effect on the rate ,but have no improvement either in the final rate compared with blank sample. So adding in additives such as salt has an effect on speeding up the rate of dyeing and improving the up-taking rate to a certain extent with a reasonable control of dosage and time.

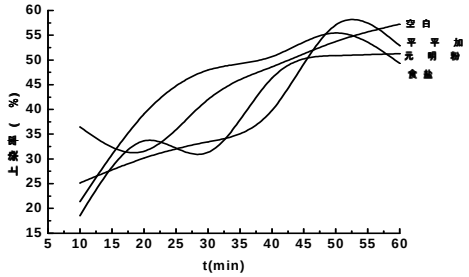

Figure 17. the influence on dye uptake rate with different auxiliaries

3.3 Results and discussion of phosphine tanned leather

3.3.1 determination of dye up-taking rate on phosphine tanned leather by acid and basic dyestuffs

Adjusting pH of phosphine tanned leather through adding in acetic acid or sodium bicarbonate for 1 hour before dyeing, then adjusting pH of dye bath to be the same value as leather .Dyeing with different basic dyestuffs or acid dyestuffs by group, other fixed dyeing conditions: T=40ºC, dosage =2%, F=2, t=60 min.

Table 18. The dyeing performances of different dyes at the same conditions

Dyestuff	pH before dyeing	pH after dyeing	DR at 10 min /%	Final DR /%	S	L	Degree of penetration			
							20 min	40 min	60 min	After drying
AF135	4.05	3.81	71.1	98.2	N	G	S	1/4	1/4	S
NGS	5.02	4.96	70.7	98.3	N	G	S	1/4	1/3	1/3
N3G	5.02	4.91	91.9	97.9	N	G	S(L)	S	S	S
RL	5.02	4.94	87.7	96.9	N	G	S(L)	S	S	S
Basic black ATT	5.08	4.87	72.9	86.8	N	G	1/2	AF	F	F
Safranine	4.02	3.91	28.4	72.5	N	G	S	1/2	F	F
Alkali blue	4.04	3.99	39.6	57.2	N	G	F(L)	F	F	F
Basic rhodamine	5.58	5.47	38.0	49.5	Deep	G	F	F	F	F

N=Normal, G=Good, S=Surface, F=full, AF=Almost full, DR=Dye uptake rate, L= leveling , L=Light

Table 18 shows that, under the same dyeing condition, acid dyestuffs reach a high dye up-taking rate at 10 min, but only the surface is dyed even after 60 min except for acid black ATT. This is because acid dyestuff is negative charged while phosphine tanned leather is positive charged which causing a quick combination between strong powered acid dyestuff and collagen of leather surface resulting in a poor dye penetration. The dyeing performance of acid black ATT is similar to basic dyestuff, and the reason needs a further research. Dyeing performance of basic dyestuffs are basically the same which is much better in term of penetration than acid dyestuffs under the same condition, and

even dyed.

So it's determined that basic dyestuff is appropriate under this experimental condition comprehensively considering with penetration, final dye uptake rate, shade and color uniformity.

3.3.2 Effect of pH on the dyeing performance

Dyeing conditions with basic dyestuff: T=40ºC, dosage=2%, F=2, t=60 min. Adjusting pH of phosphine tanned leather to different value through adding in acetic acid or sodium bicarbonate before dyeing, then adjusting pH of dye bath to be the same value as leather, then dyeing.

Table 19. The dyeing performances of Basic peach red at different pH

No.	pH before dye	pH after dye	DR at 10 min /%	Final DR	S	L	Degree of penetration			
							20 min	40 min	60 min	After drying
1#	3.00	2.91	25.3	60.1	N	G	1/2	1/3	1/3	F
2#	3.51	3.35	36.33	68.33	N	G	1/3	AF	AF	F
3#	4.02	3.91	28.4	72.5	N	G	S	1/3	F	F
4#	4.49	4.30	39.3	66.92	N	G	1/3	AF	F	F
5#	5.06	4.90	26.1	65.0	N	N	S	1/3	AF	F
6#	5.52	5.45	32.5	55.43	N	N	S	1/2	F	F

N=Number, S=Surface, F=full, AF=Almost full, G=Good, N=Normal, DR=Dye uptake rate, L= Leveling

Table 20. The dyeing performances of Basic blue at different pH

No.	pH before dye	pH after dye	DR at 10 min /%	Final DR	S	L	Degree of penetration			
							20 min	40 min	60 min	after dry
1#	3.01	3.05	35.9	57.5	N	G	F(L)	Full	Full	Full
2#	4.04	3.99	39.6	57.2	N	G	F(L)	Full	Full	Full
3#	4.53	4.59	50.9	54.9	N	G	F(L)	Full	Full	Full
4#	4.98	4.96	32.9	64.4	N	G	Full	Full	Full	Full
5#	5.53	5.3	71.5	81.8	Deep	N	Full	Full	Full	Full

N=Normal, G=Good, F(L)=full(Light) , DR=Dye uptake rate, S=Shade, L= leveling

It's not easy to observe the penetration of alkali blue. It permeates through leather quickly in a light shade and then gets deeper gradually. So the penetration can't be described accurately.

Table 19 and Table 20 show that dye uptake rate of Safranine and alkali blue has a tendency of elevation, color shade becomes deeper, and the color uniformity gets worse along with pH elevation, which shows that high pH prefers to promoting penetration of dyestuff rather than dyeing evenly. It's determined that dyeing pH 5.0 is the best value in this experiment by comprehensively considerated with penetration, final dye up-taking rate, color shade and color uniformity.

3.3.3 Effect of temperature on the dyeing performance

Experimental conditions: pH=4.5~5.3, dosage=2%, F=2, t=60 min. Dyeing at different temperature and inspecting the dye uptake rates every 10 min.

Table 21. The dyeing performances of Basic dyestuff at different temperature

Dyes	T/℃	DR at 10 min /%	Final DR /%	S	L	Degree of penetration			
						20/min	40/ min	60 /min	After dry
Alkali blue	30	49.4	54.7	N	G	F(L)	F(L)	Full	Full
	40	39.6	57.2	N	G	F(L)	F(L)	Full	Full
	55	72.7	75.9	N	N	F(L)	F(L)	Full	Full
Safranine	30	51.7	53.5	N	G	F(L)	F(L)	Full	Full
	40	28.4	72.5	N	G	Surface	1/3	Full	Full
	55	64.8	72.0	N	G	F(L)	Full	Full	Full

T=Temperature, N=Normal, G=Good, F(L)=full(Light) , DR=Dye uptake rate, S=Shade, L= leveling

Table 21 shows that both of alkali blue and Safranine show a good permeability during 30°C~55°C, but the dye does not permeate as fast as other two cases at 30°C. The dye up-taking rate reaches maximum at 55°C, then 40°C, 30°C last. In terms of color uniformity, dyestuffs show the best performance at 40°C, 55 last °C. It's determined that 40°C is the appropriate dyeing temperature in this experiment referring to the rate of dyeing and final dye up-taking rate.

Table 22. The dyeing performances of acid dyestuff at different temperature

dyestuff	T/℃	DR at 20 min /%	DR at 40 min /%	Final DR/%	S	L	Degree of penetration		
							20 min	40 min	60 min
Acid black ATT	30	83.1	90.3	93.2	N	G	Surface	1/2	1/2
	40	80.9	82.5	87.2	N	G	2/3	Full	Full
	55	87.0	90.9	92.2	N	N	AF	Full	Full

T=Temperature, N=Normal, AF=Almost full, DR=Dye up-taking rate, G=Good, S=Shade, L= leveling

Table 22 shows that the shade of acid black ATT is normal at the three temperatures and the color uniformity is relatively good at 30°C and 40°C while lightly uneven at 55°C. The rate of penetration rises along with the promotion of temperature, and the rate at 40°C is appropriate which is also good for color uniformity. The final dye up-taking rate reaches maximum at 30°C, 40°C last, but the dye up-taking rate of 30 min and 40 min at 30°C is much higher than the rate at 40°C. The main factor going against penetration is that a large number of dyestuffs combine with the surface of leather rapidly. So, 40°C is selected to be the dyeing temperature in this experiment.

3.3.4 Effect of dosage on the dyeing performance

The dye up-taking rate and degree of penetration are determined at the dosage of 2% and 3% separately, other experimental conditions: pH=5.0, F=2, T=40ºC, dyeing t=60 min .

Table 23. The dyeing performances of Cationic brilliant red at different dosage

dyestuff	dosage	DR at 20 min /%	Final DR /%	Degree of penetration	S	L
Acid black ATT	2%	80.9	82.5	Full	Light	Good
	3%	69.7	83.6	Full(Light)	Deep	Normal
Alkali blue	2%	64.5	66.2	Full	Light	Good
	3%	59.4	64.1	Full	Deep	Normal
Safranine	2%	47.2	52.5	Full	Light	Good
	3%	44.7	53.1	Full	Deep	Normal

DR=Dye uptake rate, G=Good, S=Shade, L= leveling

Table 23 shows that :acid black ATT and Safranine obtain a higher final dye up-taking rate at the dosage of 2 % while alkali blue obtain a higher rate at the dosage of 3%, but all their differences are not big at any dosage. It's observed that the shade of dyeing becomes deeper along with the dosage of dyes to increase and the color uniformity is better at the dosage of 2 %, this may because more dyestuffs are combined with leather surface at the dosage of 3 %. So, the amount of 2% of dyestuffs is more appropriate considering with general dyeing effect and economic point of view, and the dosage can be increased or decreased in practical production according to the need.

3.3.5 Effect of time on the dyeing performance

Experimental conditions: pH=4.5 ~ 5.3, F=2, T=40℃, t=100 min, dosage=2%.

Table 24. The Penetration of Cationic dyeing at different time

Time /min	20	40	60	80	100	After drying
Alkali blue	Full(light)	Full	Full	Full	Full	Full
Safranine	Full(light)	Full	Full	Full	Full	Full
Acid black ATT	1/2	Almost full	Full	Full	Full	Full

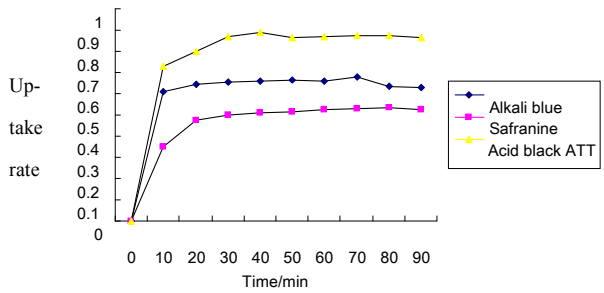

Figure 25. The Uptake rates VS time

Table 24 and figure 25 show that penetration of basic dyes are good which are better than acid dyes and all the dyes get full impregnated at last explaining extension of time is good for penetration in leather. The penetration of all the three dyes are not good enough at 20 min, and basic dyes are full

impregnated at 40 min while acid dyes aren't. All the dyes get full impregnated at 60 min and the promotion of penetration degree isn't obvious after 60 min. The dye up-taking rate of basic dyes has little change after 40 min and the rate of acid dyes becomes steady after 50 min while the rate of all the dyes decrease after 70 min instead. So the dyeing time should be lasting 60 min considering the dye up-taking rate and degree of penetration, and the time should be taken 30 min~40 min more if the fixation is taken in to account.

3.3.6 Effect of basification during the later period and color fixing agent on the dyeing performance

Table 26. The dyeing effect at fixation during the later period of dyeing

Dyestuff	Highest DR /%	Corresponding pH	Time /min								
			0	60		80	100			110	120
			pH BD	DR /%	pH AB	DR/ %	DR/ %	pH	fixing agent	DR /%	DR /%
Alkali blue	95.8	5.67	5.01	75.9	6.53	82.8	81.9	5.88	ARA=2%	92.4	95.8
Safranine	90.5	5.71	5.10	71.5	6.63	79.2	79.1	5.91	PRA=2%	89.7	91.3

DR=Dye uptake, BD=Before dyeing, AB=After basification, ARA=acrylic retanning agent, PRA=Phenolic retanning agent

Table 26 shows that it's necessary to alkalify during the later period for both of the dye up-taking rate of the two dyes improved along with basification after 60 min which proving basification is good for improving dye up-taking rate. But the rate decreases instead after achieving the peak value showing that the end pH value isn't the higher the better. The end pH value of phosphine tanned leather dyed with basic dyestuffs should be controlled around 6.5 and the time of fixation should be controlled around 30 min-40 min. Adding in appropriate retanning agent with anion after reaching end of basification could significantly improve the fixing effect making the shade of leather fuller and the dye bath further transparent. The fixing time of retanning should be controlled at 10 min~20 min.

3.4 Results and discussion of P-Al combination tanned fur

Experimental conditions: initial pH=5, L=20, T=68ºC, t=90 min, dosage=1 g/l. Adjusting pH of fur around 3.8 by adding in formic acid slowly and time after time after 60 min of dyeing, then adjusting pH of dye bath to be the same value as leather. Results are shown in table 25.

Table 25. Dyeing performance of acid dyestuffs

Dyestuff	Final dye up-taking rate/%	Shade	Degree of penetration	Color uniformity
Fur blue F-TB	86.0	Normal	Full	Good
Fur red F-SY	94.0	Normal	Full	Good

Table 25 shows that both fur blue F-TB and fur red F-SY have a good dyeing performance including shade, degree of penetration and color uniformity under the fixed conditions and both of them reach a high dye up-taking rate especially dyed with fur red F-SY which gets 94%. The results prove that the conditions taken in this experiment are appropriate for dyeing of rabbit fur.

4. Conclusions

1. Dyeing of chrome free leather is different from chrome tanned leather and basic dyestuffs are appropriate for dyeing of vegetable tanned leather and modified glutaraldehyde tanned leather.
2. The pH must be decreased by acidification before dyeing with basic dyestuffs. It‘s determined that initial pH 3.3~3.8 is the optimum condition for vegetable tanned leather while the initial pH of modified glutaraldehyde tanned leather should be adjusted to 3.5 around and the initial pH of phosphine tanned leather should be around 5.0 dyeing with both acid dyes and basic dyes.
3. The dosage of dyestuffs should be 2% and the temperature should be controlled around 40ºC, dyeing for 50 min - 60 min.
4. It’s necessary to basify in later period of dyeing with basic dyes. The final pH of veg. tanned leather should be controlled around 4.50, 4.0 to modified glutaraldehyde tanned leather and pH 6.5 is appropriate to phosphine tanned leather. The time of fixing could be controlled around 30 min-40 min.
5. Acid dyestuffs are not appropriate for dyeing of phosphine tanned leather except for acid black ATT .Because almost acid dyestuffs have a poor penetration combining with leather surface quickly which is surface dyed only .It dose not conform to requirements.
6. The average dye uptake rate of phosphine tanned leather with basic dyes is low maintaining around 60%, but easy to permeate that can be full impregnated in a short time .Basic dye uptake rate can be partly improved by adding in basification during later period and fixing agents for fixation.
7. The fixed dyeing conditions taken in this experiment such as the temperature of 68ºC, initial pH of , liquor ratio of 20, time of 90 min, dyestuff dosage of 1 g/l and adjusting pH by acidification with formic acid around 3.8 at 60 min are appropriate for fur dyeing which will show a good performance on penetration, shade and color uniformity.

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