



Introduction

The liquid sulfur dyes from our company are pre-reduced colorless solution. The reduction process is carried out under strict control, and the reducing agent and dose are filtered rigorously, making the product in ideal reducing state. Therefore, the liquid sulfur dyes reach the most stable storage state and best color development state, and can be mixed. The selection of materials is also very strict, ensuring that the dyes are environmental friendly. The dyes are in true solution state, instead of dispersed state. Therefore, they are not affected by low temperature. However, the dyes must be sealed in storage. Do not make them contact the air; otherwise, the oxidation will decrease the quality. In cold weather, if the dyes are frozen, just put them in warm environment and defreeze.

◆ Advantages of liquid sulfur dyes

1. Comparing with powder sulfur dyes, its usage is simple and it's not necessary to reduce, dissolve, and filter to dissolve the dyes, featuring high color yield, bright color, stable dyeing performance, excellent penetration, small color variation and easy control.
2. The damage degree of the greige cloth is significantly reduced comparing with powder sulfur dyes and the dyed products have high quality.
3. The compatibility among each other is excellent, ensuring the dyed products in same color.
4. The mixing is uniform and accurate, which is unparalleled by powder sulfur dyes.
5. Comparing with indanthrene and active dyes, liquid sulfur dyes feature low cost, short dyeing flow and short time consumption.
6. Comparing with powder sulfur dyes, liquid sulfur dyes feature less waste water and environmental friendly.

◆ Application

- The liquid sulfur dyes are mainly used in the dyeing of cotton fabrics including cotton yarn, cotton cloth, corduroy, and cotton blended fabrics.
- Have excellent performance in the dyeing of heavy cloth, denim, working suit and water washing style clothing.
- Suitable for leather and pulp dyeing
- Suitable for impregnating, pad dyeing, jig dyeing, etc.

Appendix I: Development of Sulfur Dyes

1. Introduction of sulfur dyes

Since the first commercial sulfur dye was researched by the French scientist Vidal in 1893, it had been widely used in the dyeing of cellulosic fibers because of its low price and simple dyeing method. The sulfur dyes are organic compounds containing nitro group and amino group, and most are reacted with sulfur and sodium sulfide in high temperature. Its molecular structure contains nitrogen, but the detailed chemical structure is not clear yet. It is represented in R-S-S-R. It is insoluble in water and needs to be reduced to colorless compound and dye the cellulosic fibers, which is similar to reduced dyes. These dyes provide excellent fastness against water washing and sunshine. By now, sulfur dyes are the best one in dyeing deep colors, low price and high fastness. Due to the improvement of environment protection and insufficient chromatogram of sulfur dyes, the application drops in recent years. Along with the development of liquid sulfur dyes and their application potential in denim, the application of the new liquid sulfur dyes is popular again.

2. Category of sulfur dyes

- (a) Powder: the earliest type
- (b) Soluble powder: still needs to be reduced to colorless compound to have affinity
- (c) Slurry: dispersed slurry; also needs to be reduced
- (d) Reduced liquid: reduction isn't needed; have strong affinity

3. Difference between powder and reducing liquid dyes

A. Powder:

Advantage: low price

Shortages:

- (a) Instable: the automatic oxidation quality deteriorates rapidly in the air and spontaneous combustion may occur because of overheating
- (b) Have chromatophilia only reduced to colorless compound in alkali liquor. The reduction is usually carried out with expensive caustic soda and rongalite, or cheap sodium sulfide.
- (c) Shortage of sodium sulfide: the purest products in the industry still have quite a few iron sulfides. It generates black sediment in water, causing color spots, or dyes accumulate on cloth.
- (d) The dissolution consumes time and thermal energy; the operation is complicated and the solution is unstable; in addition, whether it is completely soluble is uncertain.
- (e) The solubility and reduction of every dye are different, and it is easy to cause chromatic aberration.

B. Liquid:

Advantage: immediate dye; the quality is monitored by device, making the dye factory get stable and convenient liquid dye; thus the chromatic aberration is eliminated when dyeing, making the dye factory save time and get excellent dye solution.

- (a) The color is brighter than powder
- (b) The fastness is better than powder



Instructions for Liquid Sulfur Dyes

- (c) The alkali sulfide isn't necessary in reduction state; add appropriate assistant to dilute and then dye directly.
- (d) Have excellent affinity with cellulosic fibers and it is possible to dye in cold solution and hot solution.
- (e) The dyeing color is deeper than powder and features high affinity, high repeatability and less chromatic aberration.
- (f) The storage stability is high and can be stored for 3-5 years due to its appropriate alkalinity and reducing agent.
- (g) Save time and labor in storage and operation.
- (h) In continuous dyeing, it is possible to adjust the concentration at any time and it is not necessary to reduce temperature in cold bath pad dyeing (the powder needs cooling after dissolving).
- (i) Suitable for all types of dyeing machines.

4. Dyeing features of sulfur dyes

- (a) Quality standard: water washing fastness: higher than level 4; solarizing fastness: medium – deep level 6
The covering for dead cotton is better than reactivity; the leveling is poor.
- (b) Friction fastness
The sulfur dyes have the problem of wet friction. To solve this problem, wash sufficiently before oxidation until the pH value is close to neutral to ensure all chemical agents and dyes are cleared before oxidation.
- (c) Oxidation: Each dye has different oxidation degree and the appropriate oxidation could ensure high fastness. Therefore, please select oxidant carefully.
- (d) Poor leveling
Pay attention to the dyeing process and add appropriate leveling agent to eliminate the problem of leveling.
- (e) It is possible to strip color with H₂O₂ (35%) 6-10% in refined mode.
- (f) Embrittlement problem
In high temperature and humidity environment, the dyed fibers have a little sulfuric acid if sulfur dyes are retained, and thus cause embrittlement. To eliminate the embrittlement problem, wash sufficiently before and after oxidation to make the finished products have alkalescence. The brittle resistance solution also can be used to solve this problem. The cation is soft and will cause embrittlement due to its weak acid. Therefore, please be careful to use softener.

5. Storage

Since it is compound in reduction liquid, please pay attention to the chemical balance during manufacturing. The objective is to get appropriate strength and long term stability. Therefore, please keep it in sealed state if it is left unused.

When the sulfur dyes contact acid, the chemical reaction will occur and generate H₂S gas.



Instructions for Liquid Sulfur Dyes

Excessive H₂S is fatal. Therefore, the barrel used to weigh the dyes must be washed to avoid acid. Clean with water if there is acid substance. The rongalite and sulfur dyes will also generate H₂S. Therefore, if there is acid substance, please add acid substance to prevent H₂S gas.

6. Application of different dyeing methods

- A. Bobbin and beam dyeing machine: at present, liquid vulcanization is common (vulcanization isn't suitable for bobbin dyeing before). Precautions: 1. Uniform bobbin density; 2. Soft water (Ca, MgPPM below 225); 3. Refine properly to provide good infiltration; 4. Understand the performance of the dye; 5. Wash thoroughly before and after oxidation (use overflow water to wash to below pH8); 6. Good oxidation control; 7. Appropriate after treatment (pay attention to softener).
- B. Warp yarn continuous dyeing: warp yarn (coarse yarn) mainly used to dye denim. In recent years, the productivity of denim is 5 billion meters. Due to fierce competition, most dye factories use liquid sulfur dyes to reduce cost and also maintain the special requirement of denim, i.e. washing more, fading more and brighter color.

Characteristics of reduced sulfur dyes:

1. Deploy different chromatic lights.
 2. Provide the effect of washing more, fading more and brighter color.
 3. Dye deep colors.
 4. Simple operation and easy control improve the operating speed. The stopping time is short during changing colors.
- C. Reel dyeing: this method is most appropriate for small cloth. The method and precautions are same to common sulfur dyes. Generally, the cloth edge usually has red light in reel dyeing. To prevent this problem: 1. Reduce the dyeing temperature; 2. Reduce cloth reeling amount; 3. Reel in the cloth uniformly; 4. Add antioxidant. It is better to use mirabilite than using salt, because industrial salt contains calcium, magnesium and impurities that will affect the fastness of the dyeing products.
- D. Injection type dyeing machine: Low bath ratio dyeing machine is used to save energy. The liquid sulfur dyes are used to dye cotton cloth with injection dyeing machine. The liquid sulfur dyes can be added to dye jar without dissolving or mixing. It doesn't require additional water to dissolve to dye deep color, which is very important for low bath ratio machines. Follow the dip dyeing method to operate. Pay special attention to the problem of foam. Due to the quick flow of the dyeing machine and shearing force of strong pump, the foam problem in bath is the typical difficulty of injection dyeing machines. Using appropriate antifoam is critical for dyeing.
- E. Continuous dyeing: Advantages of reduced sulfur dyes: (1) the fabric surface of the dyed products is smooth; (2) chromatic differences enable random color matching.
- ### 7. Conclusion
- Due to the low price, convenient operation and excellent fastness, the liquid sulfur dyes are more and more popular in the dyeing industry. Please understand its features and use

properly to become outstanding in the dyeing industry and create high profits.

Appendix II: Application of liquid sulfur dyes in dyeing of denim

1 Development of denim

The denim has been developed. The productivity of denim has reached 5 billion meters and the demand is still increasing. In the countries that favor denim (e.g. US), every consumer has at least jeans. Chinese consumers also like jeans. Along with the strengthening of leisure philosophy, the consumption of jeans is increased rapidly. It is expected that the total amount will exceed US before long. Therefore, the production of denim becomes very important.

China has become the world factory and the same case is also applicable to the production of denim. In recent years, the productivity is increased rapidly and competition among manufacturers becomes fierce. To pursue more bigger market share and higher profits, they develop new technology, high added value and high quality products. In structure, it develops to light, thin, chiffon, jacquard weave and interweaving; in fibre, it develops to multi-varieties; in dyeing effect, more varieties like blue/black, blue/brown, and dyed multicolor jeans are developed in addition to deep blue and intermediate blue. To have the straightforward, antique, and peculiar styles, many new treatment technologies are also applied. Among these new technologies, the sulfur dyes that have similar fastness and performance with indigo have become the trend of denim.

2 Dyeing equipment of denim

The dyeing of denim is special. Through dyeing of large quantities of integrated warp, it is weaved to cloth with white weft through slashing. The machine for warp dyeing is large and complicated. There are mainly two types of warp dyeing machines in China.

The first is warp sheet dyeing machine. This method was developed in 1934 and can be combined to slurry dyeing combined machine with slashing process. The dyeing machine has 11 slots generally, including wetting, dyeing, washing and oxidation. The slurry dyeing combined machine features simple process and low investment. However, its leveling is not as good as rope dyeing machine and its productivity isn't as high as rope dyeing machine. Most dyeing machines are this type.

The second type is rope dyeing machine (or ball warping dyeing machine). This dyeing method has 160 years' history and this type of dyeing machine features high speed and large productivity. Because the warps are dyed in ropes, they have good squeeze penetration and high leveling quality. However, it also has the disadvantages like large equipment investment and high labor cost due to more processes and long flow. This production line is mainly made by US Morrison Textile Machinery Company and Japan Tenman Iron Works.



Instructions for Liquid Sulfur Dyes

- 3 Application of liquid sulfur dyes on denim
3.1 Differences between liquid and powder sulfur dyes

Item	Liquid sulfur dye	Powder sulfur dye
Operation	Dye in jar directly	Dissolve with alkali sulfide first
Environmental protection	Beneficial	None
Content of sulfide	Low	High
Odor	No	Yes
Generation of hydrogen sulfide	Difficult	Yes
Reduction	Controller, uniform	Difficult to be controlled
Alkalinity	Low	High
Water consumption	Low	High
Dyeing depth (warp dyeing)	High	Common
Fastness (warp dyeing)	Excellent	Common
Initial adsorption ratio and instant dyeing ratio	Controllable	High
Leveling	Pay attention in dyeing	Pay attention in dyeing
Adjusting depth or light color	Easy	Complicated

3.2 Dyeing process

Wetting - padding liquid - air infiltration – washing – oxidation color fixing – washing - drying

3.2.1 Formula of dye vat

Dye and assistant	Dye vat g/l	Assistant vat g/l
Chelate dispersing agent HY-102	4-5	4-5
Strong leveling agent HY-210	3-4	3-4
30% sodium hydrate	100	100
Glucose	40	50
Dye	X	Y

Note: The dye contents of dye vat and assistant vat depend on the variety of dyes. Their relationship is feeding coefficient.

3.2.2 Formula of oxidation tank

Drug name	Oxidation tank g/l	Assistant vat g/l
Acetic acid (80%)	5-7	50
Hydrogen peroxide (30%)	5-7	50

- 4 Note



Instructions for Liquid Sulfur Dyes

- 4.1 Temperature of dye vat: 70-90°C
- 4.2 Oxidation temperature: 70°C; pH value of oxidation tank: 4-4.5
- 4.3 The chelate agent in the dyeing formula is used to prevent calcium, magnesium and other metal ions generating insolvable complex with sulfur dyes and causing dye spots on the fabrics. To dye denim, raw yarns are usually used. However, the content of metal ions in raw yarns is very high; therefore, it is necessary to add chelate agent. Since the leveling of sulfur dyes is poor, it is necessary to add certain amount of leveling agent.
- 4.4 The wetting agent should be alkali resistant anion type. The strong leveling agent HY-210 is a kind of anionic, low foaming and non-retarding composite. The denim is dyed with basic yarn, which has a worse wetting degree than refined yarn. If the penetrant is insufficient, it will cause uneven dyeing and stripes. In addition, the basic yarns have different kinds and wetting degrees. For example, ring yarn requires more penetrant than rotor spun yarn.
- 4.5 To match color, it is necessary to dilute the dyes in 1:2-5 ratio and then mix them together. Blue antioxidant (special leveling agent for sulfur dyes) requires higher amount.
- 4.6 It is simple and convenient to use liquid sulfur dyes for warp dyeing. The premise is to trim the dyeing process according to the specific condition of the machine to exert the performance of the dye. More importantly, the dyeing factories using liquid sulfur dyes will get stable and uniform dyeing solution and a safe environment, and also save the cost of waste water treatment.

5 Appendix: supplementary rate

Dyeing rate	Slow	Intermediate slow	Intermediate	Intermediate fast	Fast
Supplementary rate	1.05-1.2	1.1-1.3	1.2-1.5	1.3-1.7	1.4-2.0
Light color 25g/l	Red LGF	Yellow brown	Brown, olive, green, black	Red brown, black, dark green	Red brown, blue, royal blue
Deep color > 100g/l	Black, red brown, orange, green, deep brown	Yellow, red, olive, yellow brown, blue, navy blue, bright green	Dark green, brown, blue, deep blue, navy blue, red brown	Green	

Note: This table is for reference only. Modify according to the specific condition of dyeing factories and experiences of operators, as well as speed, temperature, dyeing rate, bath ratio, dyeing depth, textile thickness, etc, and depended on dyeing effect finally.



Operation Precautions

- To match color, dilute the liquid dye to 2-3 times with soft water and then mix
- Test the water quality and add water softener according to the water hardness. If the water hardness is too high, the dye will settle and cause color mess easily.
- Add assistant agent and dyes in sequence, making the performance of the dyes optimal
- Be careful and test before using assistant agents.
- The textile must have good capillary effect after treatment; the pH value of the cloth is 7-8; avoid phenomena like alkaline spotting, unclean desizing and uneven pH value.
- The washing after dyeing is critical. Wash with overflow water and the raffinate shouldn't be cleared once.
- Observe and adjust during oxidation to avoid insufficient oxidation or excessive oxidation.

Safety Precautions

- Wear protective glasses and gloves when carrying the dyes.
- If the eyes contact the dyes, wash with clean water immediately and go to see your doctor.
- Keep the dyes away from acid substance or oxidant, because they will deteriorate if contact these substances.

Packaging and Storage

- 25kg and 30kg plastic drum, or according to the customers' requirements.
- Seal and keep away from acid and oxidants
- Storage temperature: 5-35°C; if there is crystal in winter, heat to dissolve the dyes
- Be careful when carrying and avoid damaging the packaging drum and cause leakage.

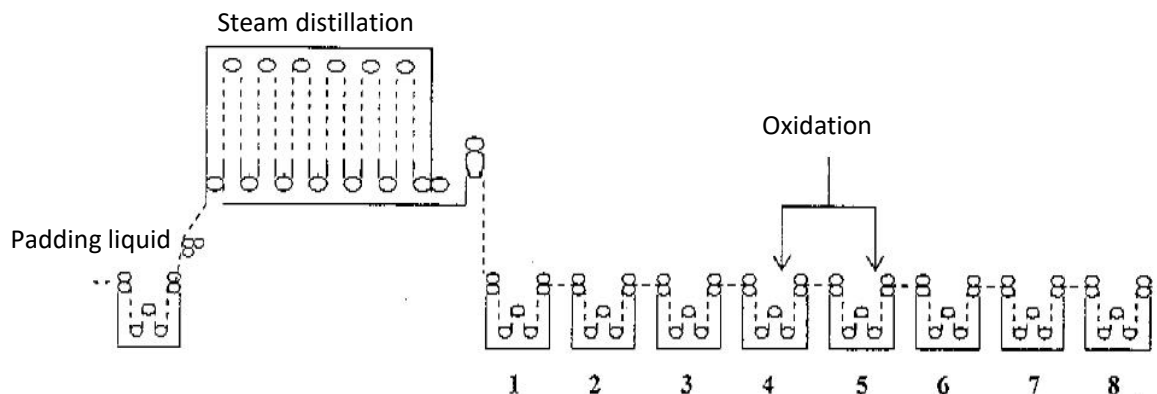


Exemption Clauses

This manual and the oral and written technical opinions of our company come from our sincerity, but we won't make warranty. The users also need to test the products that we provide to check whether they are suitable for the planned process and purpose. Especially, the users need to test the performance according to their specific usage, equipment condition and application condition. The technical data that we provide are for reference only. The users should be responsible for the products that they make according to our technical opinions.



Pad Steaming Process



I. Formula of groove

HY series dye	X g/l
30% caustic soda	50 g/l
Glucose	30 g/l
HY-102	5 g/l
HY-210	5 g/l

II. Process flow

- 40-70°C padding dye solution, padding surplus rate: 70-80%
- Steam distillation (102-104°C saturated vapor, 60 seconds)
- Washing in groove 1, 2, 3 (groove 1 – 50°C; groove 2 – 50°C; groove 3 - 50°C)
- Oxidation groove 4, 5 (see oxidation process)
- Washing in groove 6 (50°C)
- Soaping in groove 7 (90°C)
- Washing in groove 8 (60°C)
- Drying

III. Procedure of preparing dyeing solution

- (1) Add half of required water in 25-30°C
- (2) Add HY-102
- (3) Add glucose
- (4) Add HY-210
- (5) Add dyes; for color matching, dilute the dyes respectively and then add
- (6) Add 30% caustic soda
- (7) Add water to required level

IV. Oxidation process

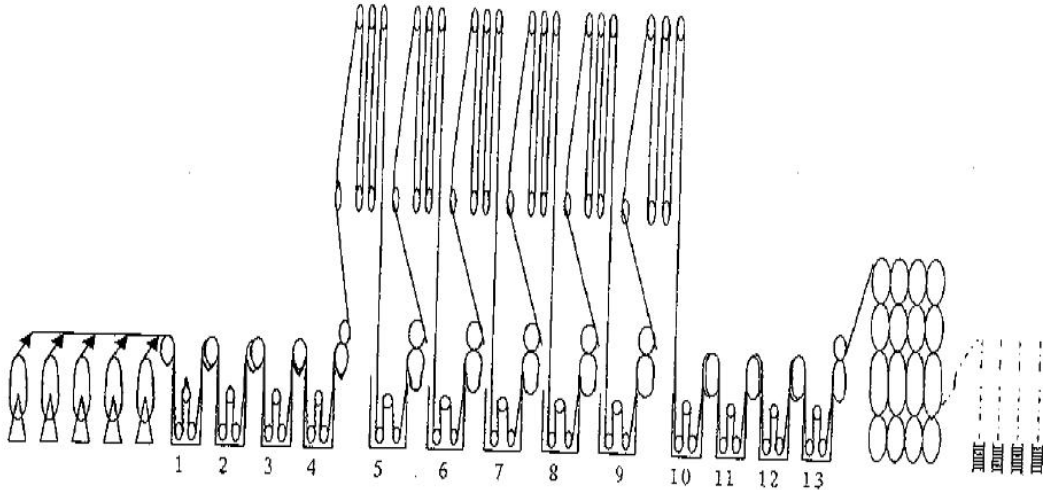
Formula	Consumption g/l	pH value	Temperature °C	Time s
Hydrogen peroxide (30%)	5-7	4-4.5	50	45-60
Acetic acid (30%)	5-7			

Instructions for Liquid Sulfur Dyes



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SHINE IMP AND EXP CO., LIMITED

Denim Process



Add the following items into the dye vat in sequence in 60-90°C

4-5g/l	HY-102
5-10g/l	HY-210
50g/l	30% caustic soda
30-40g/l	glucose
Xg/l	HY series liquid sulfur dyes

Washing in dye vat 2, 3, 4

Oxidizing in dye vat 10

Washing in dye vat 11, 12, 13

Oxidation process

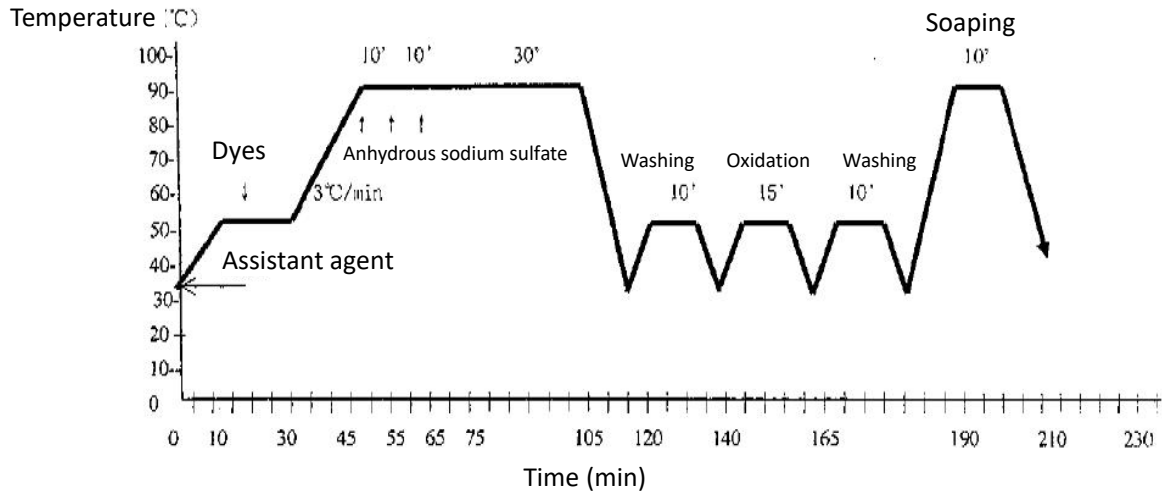
Formula	Consumption g/l	pH value	Temperature °C	Time s
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Acetic acid (30%)	5-7			

Instructions for Liquid Sulfur Dyes



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Dip Dyeing Process



Add the following items in sequence in 30°C

- 1-2g/l HY-102
- 1-2g/l HY-210
- 10g/l 30% NaOH
- 5 g/l glucose
- Xg/l HY series liquid sulfur dyes

Heat to 60°C

Add dyes in 20 minutes

Heat to 75°C

Retain temperature for 10 minutes

Add 30-40g/l anhydrous sodium sulfate in 2-3 times and retain the temperature for 30 minutes

Reduce the temperature and wash with overflow water

Wash for 10 minutes in 50°C

Oxidize (see Oxidation Process)

Wash for 10 minutes in 50°C

Soap for 10 minutes in 90°C

2g/l foamless soaping agent HY-190

Wash to normal temperature

Enter after treatment process

Oxidation process

Formula	Consumption g/l	pH value	Temperature °C	Time s
Hydrogen peroxide (30%)	2-4	4-4.5	50	15-20
Acetic acid (30%)	2			

Instructions for Liquid Sulfur Dyes



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Jig Dyeing Process

Add the following items in two times in 60°C

1-2g/l	HY-102
1-2g/l	HY-210
20g/l	30% NaOH
10 g/l	glucose
Xg/l	HY series liquid sulfur dyes

Add dyes in two times in 60°C

Heat to 75°C (heat to 95°C for black)

Add 30-40g/l anhydrous sodium sulfate in 2 times

Retain the temperature

Wash clean with overflow water

Oxidize for two times (see Oxidation Process)

Wash for two times

Soap for two times in 90°C

2g/l foamless soaping agent HY-190

Wash

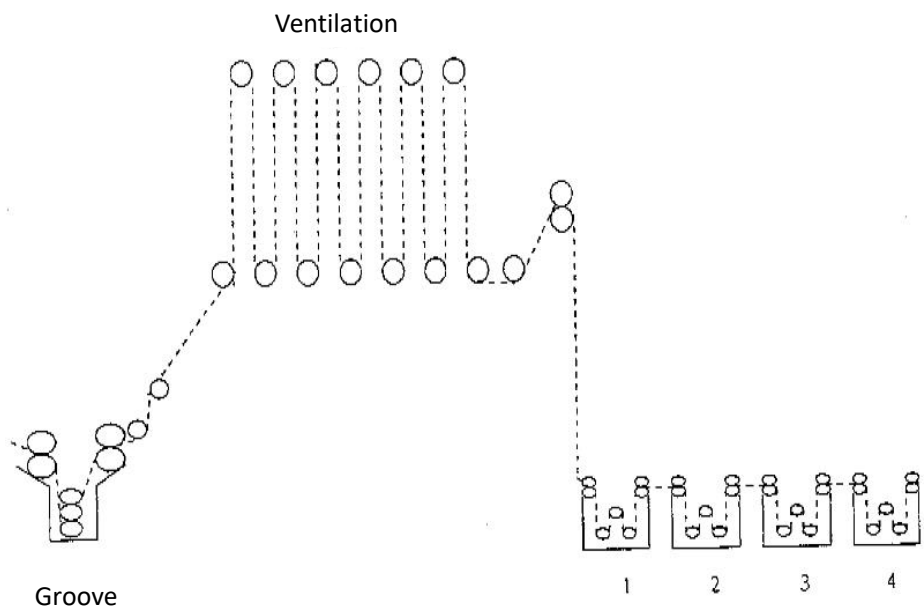
Oxidation process

Formula	Consumption g/l	pH value	Temperature °C
Hydrogen peroxide (30%)	2-4	4-4.5	50
Acetic acid (30%)	2		



Pad-oxygen Process

(suitable for washer wrinkle fabric)



- 60-90 °C padding dye solution
- | | |
|--------|------------------------------|
| 5g/l | HY-102 |
| 5g/l | HY-210 |
| 50g/l | 30% NaOH |
| 20 g/l | glucose |
| Xg/l | HY series liquid sulfur dyes |

Ventilate for 30-60 seconds

Oxidize and fix color in groove 1, 2 in 60 °C

Oxidation temperature: 55-65 °C ; oxidation time: 30-60 seconds; PH value of oxidation solution: 4.5-5.0

Formula of oxidation color fixing solution:

- | | |
|--------------------------------------|----------|
| (1) 30% hydrogen peroxide | 15-20g/l |
| (2) Acetic acid | 15g/l |
| (3) Aldehydeless coloring stabilizer | 25g/l |

Wash in groove 3, 4

Temperature: 60-70 °C

Instructions for Liquid Sulfur Dyes



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Product Environment Protection Certificate Guarantee Letter

Supplier: Innuovo Chem-dye Co., Ltd., Hengdian Group.

We guarantee that all the liquid sulfur dyes made by our company are new dyes that can be used to replace restricted materials. They do not contain the 24 carcinogenic aromatic amines expressly stipulated by the German government and EU, and azo-dyes that won't crack and release 22 carcinogenic aromatic amines; do not contain allergic dyes; do not contain carcinogenic dyes; do not contain acute toxic dyes; do not contain environment hormone; do not contain metal heavy ions; do not contain absorbable organic compound; do not contain and won't release formaldehyde; the application in textiles accords with the requirements of German BCO-TEX STANDARD 100 and the performance accords with the international requirement on textiles.

Hereby certify