



TRIBRITE MIDNIGHT

Process For Black Trivalent Chromium Plating

INTRODUCTION

Tribrite Midnight is a decorative chromium plating process which produces a smoky to black finish. It is based on trivalent chromium complexes and is a substitute for traditional hexavalent chromium plating processes.

BENEFITS

- Provides the deepest, darkest colour in the industry
- Colour can be adjusted from a light smoky, to a deep, dark black
- Eliminates burning and whitewash associated with hexavalent processes
- Greatly reduces waste treatment costs

SOLUTION MAKE-UP

It is essential that the tanks to be used for Tribrite Midnight are thoroughly cleaned and leached before any chemistry is introduced. If in any doubt as to the cleaning procedure please contact PMD Chemicals Technical Department.

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|--------------------------------|-------------------------|
| 1. Tribrite Conductivity Salts | 300 g/l |
| 2. Tribrite Make Up | 100 ml/l |
| 3. Tribrite Replenisher | 60 ml/l |
| 4. Tribrite Midnight | As required for colour. |
| 5. Tribrite Wetter | 4 ml/l |
| 6. Tribrite Enhancer | 1 ml/l |

1. To clean plating tank install the special graphite anodes and titanium hangers. It is recommended that the buss bars be heavy nickel plated before installation. After the titanium hangers are installed to the buss bar, wrap the bussing with plastic tape or cover with appropriate inert material to minimize copper contamination from the copper bussing.
2. Install the heating and cooling coils. If the cooling coils are titanium, connect the coils through some high impedance wire so they are anodically protected.
3. Regenerate the Ion Exchange Resin then connect the system to the plating tank.
4. Fill tank with water.



5. Check agitation to ensure it is uniform.
6. Turn on Ion Exchange system and check flow rate then turn off and turn flow valves off.
7. Check heating and see what the heat up time of solution to 60°C is. Then turn on cooling if equipped to see if it works properly.
8. Lower pH to 2.5 with hydrochloric acid.
9. Allow solution to stand for eight hours at operating temperature of 32°C. This will leach the equipment and tank. Run the Ion Exchange system for 1 hour.
10. Discard leach solution.
11. Fill the plating tank 1/3 full with water (D.I. water should be used if available).
12. Turn on the heating and air agitation and heat the solution to 60 – 65°C.
13. Using air agitation, slowly add 300 g/l of the TRIBRITE CONDUCTIVITY SALTS. Solution temperature will drop as the salts are added. Bring the temperature back up to 60 – 65°C. If the material is added too fast it may settle to the bottom and not dissolve properly. Check bottom of tank to ensure all the material is dissolved before proceeding to the next step. It takes approximately 2 hours at the high temperature to completely dissolve all the powder salts.
14. Add 100 ml/l TRIBRITE MAKE UP.
15. Add 60 ml/l of the TRIBRITE REPLENISHER and TRIBRITE MIDNIGHT then bring volume up to operating level, maintain heat for 4 hours.
16. Allow solution to cool to operating temperature.
17. Add 4 ml/l of the TRIBRITE WETTER then add 1 ml/l of the TRIBRITE ENHANCER.
18. Allow solution to mix for 10 minutes then check pH of the solution. Adjust if necessary.
19. Check the concentration of the chromium metal, and the TRIBRITE REPLENISHER and adjust if necessary.
20. The solution will be ready to plate parts at this point.
21. If there are any HCD or LCD defects noted then the solution will need to be dummy plated for a short time. If dummy plating is needed then heavy nickel plate a steel corrugated panel and dummy plate at 9.7 amps/dm² or 90 amps/ft² for 1 hour, then plate parts to see if all defects have been removed.



OPERATING DATA

Tribrite Conductivity salts	280 – 330g/l (opt. 300g/l)
Tribrite Make Up	80 – 120ml/l (opt. 100ml/l)
Tribrite Replenisher	50 – 65ml/l (opt. 60ml/l)
Tribrite Wetter	2 – 6ml/ (opt. 4ml/l)
Tribrite Enhancer	1ml/l
Tribrite Midnight	1 – 32ml/l
Chromium (Cr+3)	20 - 23g/l (opt. 21g/l)
pH	2.3 – 2.9
Temperature	27 – 43°C (opt. 30°C)
Specific gravity	1.170 – 1.210
Cathode current density	80 – 125 asf (8.5 – 13.4 asd)
Anodes	Graphite
Anode current density	<50 asf (5 asd)
Agitation	Mild air
Deposition rate	0.05-0.1µm/min at 10 asd

EQUIPMENT

Tanks	Steel lined with PVC or Polypropylene (Use of tanks previously used for hexavalent chrome <u>must</u> be relined. Lead lined tank must not be used.)
Heaters	PTFE, titanium with thermostatic control.
Anodes	Graphite anodes (bottom of anode 15-20cm from bottom of tank) with titanium hooks constructed to ensure best electrical contact. (the hook should be constructed to ensure the top of the anode is immersed in the liquid for 2-3 cm). Anodes should be checked regularly to ensure good contact. Anodes should not be removed for 30 minutes after end of plating to prevent chlorine emission, (which has absorbed into anodes.) Copper anode rail or bus bars should be nickel plated or wrapped with plastic waterproof tape to avoid possible copper contamination from exposed bars.
Air agitation	Uniform mild agitation below the cathode area. Too much agitation results in reduction of chrome coverage. Too little results in non-uniform thickness.
Ampere Hour Meter	Recommended for optimum control of additives, which are best added regularly in small amounts on an ampere-hour basis.
Rectifiers	A minimum of 12V is recommended in most operations.
Filtration	Filter pumps must be constructed of acid resistant materials. Size and type depends on purification method.
Ion exchange	Wherever possible an ion exchange unit to remove metallic impurities is recommended.



MAINTENANCE AND CONTROL

TRIBRITE CONDUCTIVITY SALTS

TRIBRITE CONDUCTIVITY SALTS are used for make-up and replenishment of the solution from drag out. It provides conductivity to the bath. Additions of TRIBRITE CONDUCTIVITY SALTS should be made slowly to minimize undissolved salts in the bath.

The addition of 21 g/l of the TRIBRITE CONDUCTIVITY SALTS will raise the specific gravity 0.01 units.

High concentration of TRIBRITE CONDUCTIVITY SALTS can result in crystallization if the solution temperature is too low.

Low concentration of TRIBRITE CONDUCTIVITY SALTS will result in lower conductivity and may require use of higher voltages to maintain the same current density.

TRIBRITE MAKE UP

TRIBRITE Make Up is used for make-up or when the solution is low in chromium concentration. Additions larger than 6 ml/L should be made in several small increments. If a very large addition must be made then it may be helpful to heat the solution for 4 - 6 hours after the addition to properly complex the chromium.

To raise chromium - 38.6 ml/l TRIBRITE Make Up = 7.5 g/l chromium.

TRIBRITE REPLENISHER

TRIBRITE REPLENISHER is proportioned, pre-complexed and contains appropriate amounts of the chromium, complexer and other proprietary chemistry to allow simple control of the chromium complex to be plated out of the solution. TRIBRITE REPLENISHER is consumed by drag-out and electrolysis. High TRIBRITE REPLENISHER can result in some precipitation. Low TRIBRITE REPLENISHER can result in reduced plating rate.

Maintain the concentration of the TRIBRITE REPLENISHER within the specified ranges.

TRIBRITE REPLENISHER should be added at 1.6 litres per 1000 amp/hrs.

Solution is pre-complexed so large additions are not detrimental compared to competitive processes.

1 ml/l will raise the chromium concentration by approximately 0.0375 g/l and increase TRIBRITE REPLENISHER by 0.1%/vol.

TRIBRITE WETTER

TRIBRITE WETTER reduces the surface tension of the solution and improves the metal distribution of the deposit. Low concentrations can result in dark streaks. High concentrations can result in excessive foaming during electrolysis.

TRIBRITE WETTER should be added at 18-36 ml/1000 amp/hrs and should be added at least once every 4 amp/hrs/l of operation.

Concentration can be determined by measuring the surface tension.



TRIBRITE ENHANCER

TRIBRITE ENHANCER improves the current density range of the deposit.

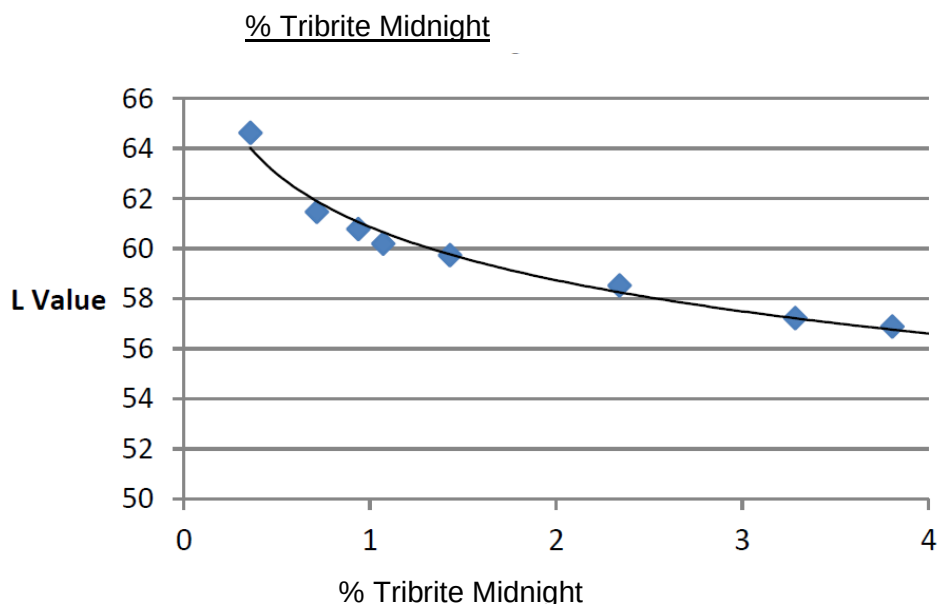
TRIBRITE ENHANCER is added at solution make-up. Further additions should only be made when advised by your PMD Chemicals Technical Department.

TRIBRITE MIDNIGHT

Tribrite Midnight produces the black colour in the deposit. Tribrite Midnight is used for make-up and replenishment. The degree of darkness can be increased by increasing the concentration of the Tribrite Midnight. Concentration of the Tribrite Midnight can be determined by measuring the degree of darkness of the deposit. The chart below gives the L-Value versus the %/volume concentration of the Tribrite Midnight. However the degree of darkness does not increase substantially over the concentration of 32 ml/l (3.2%/vol). It is there recommended that the upper limits for concentration should be 32 ml/l.

Consumption of the Tribrite Midnight depends on the concentration of Tribrite Midnight maintained in the operating solution. Lower concentrations of Tribrite Midnight such as 1 ml/l (0.1%/vol) will require an addition rate of 78 ml /1000 AH. Higher concentration of Tribrite Midnight 32 ml/l (3.2%/vol) will require an addition rate of 113 ml/1000 AH.

%/Vol Tribrite Midnight





TEMPERATURE

The process operates at 27 – 43°C, heating will be required. If production is above 0.5 amp/l or if ambient temperature is high, then cooling will be required.

High temperature will reduce the covering power.

Low temperature can result in precipitation of the salts.

pH

The pH should be maintained between 2.3 and 2.9.

Raise the pH 0.1 unit with the addition of 2 ml/l ammonium hydroxide.

Lower the pH 0.1 units with the addition of 2 ml/l hydrochloric acid.

pH adjustments will produce an artificially large change in pH that will equilibrate after a period of time.

It is also recommended pH calibration buffers bracket the pH being measured.

Tribrite PURE Ion Exchange Systems

Ion Exchange equipment is available from PMD. Consult your PMD representative for proper sizing of equipment.

Tribrite PURE Ion Exchange Resin

Obtain the special Ion Exchange resin from PMD.

ANALYSIS METHODS

TRIBRITE REPLENISHER

Reagents

5%w/v Sodium Carbonate solution

10% w/v Potassium Iodide solution

50%v/v Sulfuric acid

0.1N Sodium thiosulfate solution

0.1N Potassium permanganate solution

1%w/v Starch Indicator solution

Method

1. Pipette 1.0 ml of the filtered solution into a 250 ml conical flask. Run a blank using water in place of the plating solution. It is suggested that a blank be run at least monthly until experience dictates otherwise.

2. Add 5.0 ml of 5% sodium carbonate solution.



3. Place the flask in a boiling water bath so that the flask is generally upright and the liquid in the flask is covered by the boiling water. Heat for 15 minutes. After this time, carefully remove the flask and smell the flask for ammonia. All ammonia should be driven off but if an odour of ammonia can be detected, reheat for another 2 - 3 minutes. In any event, all ammonia must be removed before continuing.
4. Remove from the water bath, wash down the sides of the flask with 5 ml DI water. Cool to room temperature.
5. Pipette 25.0 ml of approx. 0.1 N potassium permanganate solution into the flask. Swirl to coat any precipitate on the flask walls with the mixture.
6. Again, place the flask into the boiling water bath for 5 minutes. The purple permanganate should change to brown shortly after heating.
7. Cool to room temperature.
8. Add 5 mL of 10% w/v potassium iodide solution.
9. Add 5 mL of 50% sulphuric acid and immediately titrate with 0.1N sodium thiosulfate solution until the solution turns a light yellow. Add approx. 10 drops starch indicator and titrate to a clear light blue end-point.
10. Record titre = A mls (For blank titre = B mls)

Calculation

TRIBRITE REPLENISHER ml/l = $0.606 \times (\text{ml B} - \text{ml A})$

TRIVALENT CHROMIUM

Reagents

30% Hydrogen Peroxide solution
50%w/v Sodium Hydroxide Solution
10% w/v Potassium iodide solution
50%v/v Sulfuric acid solution
1%w/v Starch solution
0.1N Sodium thiosulfate solution

Method

1. Pipette 5.0 ml of the filtered solution into a 100 ml volumetric flask and dilute to volume.
2. Pipette 5.0 mL of the solution from the flask directly to a 250ml conical flask.
3. Add 6 drops of 30% hydrogen peroxide.
4. Add 4 drops of the 50% sodium hydroxide solution.



5. Swirl tightly and insert into the boiling water bath. Maintain heat for five (10) minutes. All traces of gassing should be removed.

6. Add 5 ml 10% potassium iodide solution and mix.

7. Add 10 ml 50% sulfuric acid and immediately titrate with 0.1N sodium thiosulfate solution until the solution turns a straw colour.

8. Add 1 ml 1% starch solution and again titrate to the disappearance of the dark blue starch/iodine colour.

Calculation

$\text{g/l Cr}^{+3} = \text{mls } 0.1\text{N Sodium Thiosulphate} \times 6.78$

DISPOSAL

Dispose of in accordance with local authority requirements.

PRODUCT FAMILIES

The following products are referred to in this data sheet.

PRODUCT NAME	PRODUCT NUMBER
TRIBRITE MIDNIGHT	414009
TRIBRITE REPLENISHER	414005
TRIBRITE CONDUCTIVITY SALTS	414002
TRIBRITE ENHANCER	414007
TRIBRITE WETTER	414006
TRIBRITE PURE IEX RESIN	414008
TRIBRITE MAKE-UP	414003

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