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TriCOL™ BlackJack

Black Trivalent Chromium Plating
Process
TECHNICAL DATA
5-12-16

TriCOL BlackJack *PROCESS FOR BLACK TRIVALENT CHROMIUM PLATING*

- TriCOL BlackJack Provides the deepest darkest color in the industry.
- TriCOL BlackJack Color can be adjusted from a light smoky color to a deep dark black color.
- TriCOL BlackJack Eliminates burning and whitewash associated with hexavalent processes.
- TriCOL BlackJack Greatly reduces waste treatment costs.

OPERATING PARAMETERS

	<u>RANGE</u>	<u>OPTIMUM</u>
Temperature	27 - 43°C (80 - 110°F)	29 - 32°C (85 - 90°F)
pH	2.3 - 2.9	2.6 - 2.8
Current Density	8.5 - 13.4 Amps/dm ² (80 - 125 Amps/ft ²)	
TriCOL T-Salts 100	390 - 460 g/l (52 - 61.3 oz/gal)	415 g/l (55.3 oz/gal)
TriCOL Replenisher 300	45 - 75 ml/l (4.5-7.5% by vol.)	55 ml/l (5.5% by vol.)
TriCOL Antimist 400	2 - 6 ml/l (0.1-0.6% by vol.)	4 ml/l (0.4% by vol.)
TriCOL CD Plus 500	1.0 ml/l (0.1% by vol.)	1.0 ml/l (0.1% by vol.)
TriCOL BLACK 600	1 - 32 ml/Liter (0.1 - 3.2%/vol)	
Chromium (Cr+3)	20 - 23 g/l (2.7 - 3.1 oz/gal)	21 g/l (2.8 oz/gal)
Specific Gravity	1.21	
Agitation	Air through low pressure blower recommended.	
Anode to Cathode Ratio	1.5:1 to 2.0:1	
Current – DC	Less than 10% ripple	
Voltage	6 - 15 volts	
Deposition Rate	Approximately 0.05 - 0.10 microns at 10.8 Amps/dm ² (2 - 5 microinches/min at 100 Amps/ft ²)	
Filtration	Usually not required, proper Ion Exchange equipment is needed.	

Solution Make-Up

<u>Material</u>	<u>100 Liters</u>	<u>100 Gallons</u>
TriCOL T-Salts 100	41.5 kg	346 pounds
TriCOL Replenisher 300	6.5 Liters	6.5 gallons
Tri-COL Antimist 400	400 milliliters	0.4 gallon
TriCOL CD Plus 500	100 milliliters	0.1 gallon
TriCOL BLACK 600	Dependent on color desired	

Solution Preparation:

1. To a 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 and then connect the system to the plating tank.
4. Fill tank full with water.
 - a) Check agitation to insure it is uniform.
 - b) Turn on the Ion Exchange system and check flow rate then turn off, and turn flow valves off.
 - c) Check heating and see what the heat up time of solution to 60 degrees Celsius is. Then turn on cooling if equipped to see if it works properly.
 - d) Lower pH to 2.5 with hydrochloric acid and then add 1ml/Liter of the TriCOL Antimist 400.
 - e) 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.
 - f) Pump out the leach solution, drain the Ion Exchange system, and rinse the tank out.
5. Fill the plating tank ½ full with city water (D.I. water should be used if available).
6. Turn on the heating and air agitation and heat the solution to 60 - 65°C (140 - 150°F).
7. Using air agitation, slowly add 415 g/Liter of the TriCOL T-Salts 100. Solution temperature will drop as the salts are added. Bring the temperature back up to 60 - 65°C (140 - 150°F). If the material is added too fast it may settle to the bottom and not dissolve properly. Check bottom of tank to insure all the material is dissolved before proceeding to the next step. Usually it takes 2 hours at the high temperature to completely dissolve all of the TriCOL T-Salts 100.
8. Add 55 ml/Liter (5.5%/vol) TriCOL Replenisher 300 and the TriCOL BLACK 600 then bring tank volume up to operating level and maintain heat for 4 hours.
9. Allow solution to cool to operating temperature.
10. Add 4 ml/Liter of the TriCOL Antimist 400, then add 1 ml/Liter of the TriCOL CD Plus 500.
11. Allow solution to mix for 10 minutes then check pH of the solution. Adjust if necessary.
12. Check the concentration of the chromium metal. Adjust if necessary.
13. The solution will be ready to plate parts at this point.
14. 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 put enough area in the tank to equal approximately 25 – 50 m²/1000 liter or 1 - 2 ft²/100 gallons. 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.

Recommended Equipment

Tank or Tank Liner -	New PVC, polypropylene, polyethylene, ABS or Koroseal-lined steel.
Heaters/Cooling Coils -	Quartz, PTFE, and titanium (must be grounded or anodic).
Heaters/Chillers -	Quartz, PTFE, and titanium (must be grounded or anodic).
Racks -	Plastisol-coated copper.
Anodes -	Use TriCOL Anodes. Consult Columbia Chemical for recommendations.
Anode Hangers -	Use TriCOL Anode Hangers. Consult Columbia Chemical for recommendations.
Bus Bars -	Copper bus that is heavily nickel plated to avoid possible copper contamination. Bus bars that are exposed should be protected from solution by a plastic shield or by wrapping with plastic waterproof tape.
Ion Exchange -	Use Columbia TriCOL PURE Ion Exchange Systems.
Ion Exchange Resin -	Use Columbia TriCOL PURE Resin.

TriCOL BlackJack ADDITION AGENTS and REPLENISHMENT

TriCOL T-Salts 100

TriCOL T-Salts 100 is used for make-up and replenishment of the solution from drag-out. It provides conductivity to the bath. Additions of TriCOL T-Salts 100 should be made slowly to minimize undissolved salts in the bath. Additions should be made in several smaller increments if the additions are over 30 g/Liter (4 oz/gallon). Large additions can also be made by simply heating the solution after the addition. The heating will properly complex the chromium whenever very large additions are required.

The addition of 21 g/Liter (2.8 oz/gallon) of the TriCOL T-Salts 100 will raise the specific gravity 0.01 units. Make the additions of TriCOL T-Salts 100 prior to adding the TriCOL Replenisher 200.

High concentration of TriCOL T-Salts 100 can result in crystallization if the solution temperature is too low.

Low concentration of TriCOL T-Salts will result in lower conductivity, and may require use of higher voltages to maintain the same current density.

TriCOL Replenisher 200

TriCOL Replenisher 200 is replenished on an ampere-hour basis and replaces the chromium that is plated out of solution. TriCOL Replenisher 200 is added at a rate of approximately 435 g/1000 ampere-hours (15.3 oz/1000 ampere-hours) and should be added at least once every 3.5 ampere-hours/Liter (13 ampere-hours/gallon) of operation.

Additions larger than 7.0 g/Liter (0.93 oz/gallon) should be made in several small increments. If a very large addition must be made then it may be helpful to heat the solution after the addition to properly complex the chromium.

TriCOL Replenisher 300

TriCOL Replenisher 300 allows the chromium to be plated out of solution. TriCOL Replenisher 300 is consumed by drag-out and electrolysis. High TriCOL Replenisher 300 can result in some precipitation of the salts. Low TriCOL Replenisher 300 can result in reduced plating rate. Maintain the concentration of the TriCOL Replenisher 300 within the specified ranges. TriCOL Replenisher 300 should be added at 1.52 liters (51 fl.oz) per 1000 ampere-hours and should be added at least once every 4.5 ampere-hours/Liter (17 ampere-hours/gallon) of operation.

TriCOL Antimist 400

TriCOL Antimist 400 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. TriCOL Antimist 400 should be added at 18 - 36 ml/1000 ampere-hours (0.6 - 1.2 fl.oz/1000 ampere-hours) and should be added at least once every 4 ampere-hours/Liter (15 ampere-hours/gallon) of operation. Concentration can be determined by measuring the surface tension.

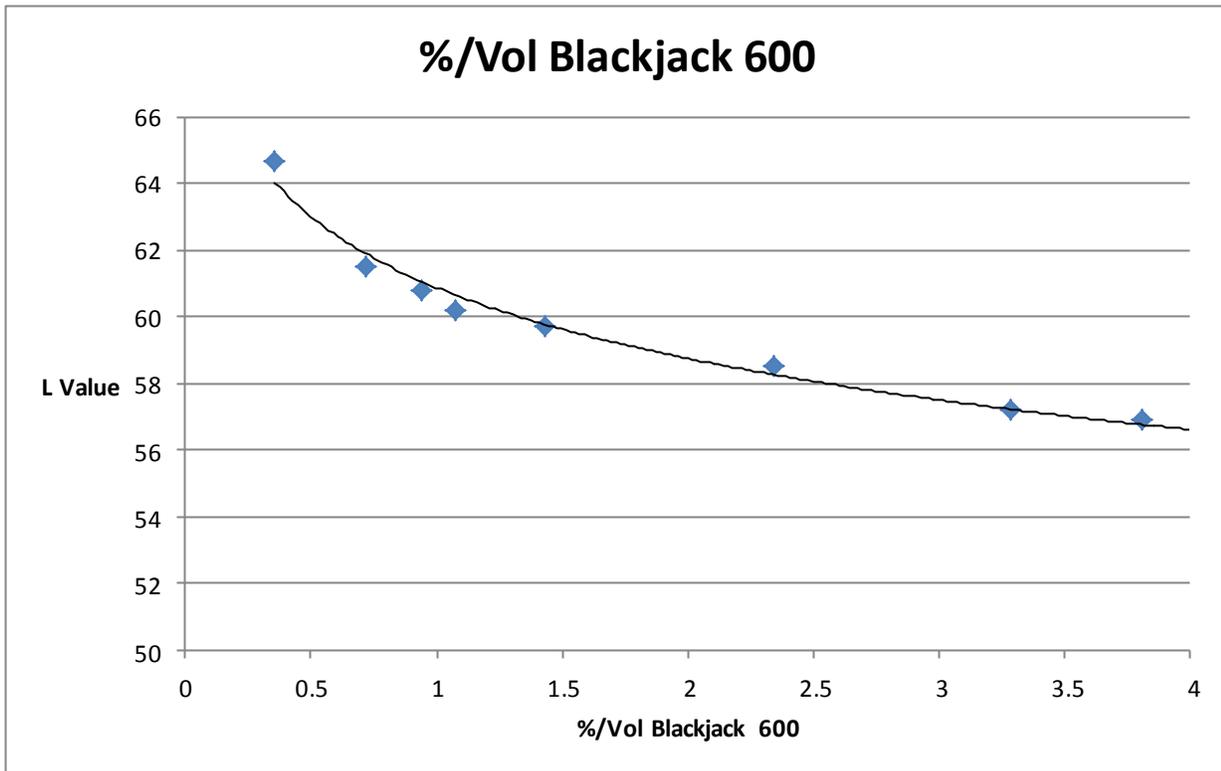
TriCOL CD Plus 500

TriCOL CD Plus 500 improves the current density range of the deposit. TriCOL CD Plus 500 is added at solution make-up. Further additions should only be made when advised by your Columbia Chemical representative.

TriCOL BLACK 600

TriCOL BLACK 600 produces the black color in the deposit. TriCOL BLACK 600 is used for make-up and replenishment. The degree of darkness can be increased by increasing the concentration of the TriCOL BLACK 600. Concentration of the TriCOL BLACK 600 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 TriCOL BLACK 600. However the degree of darkness does not increase substantially over the concentration of 32 ml/Liter (3.2%/vol). It is there recommended that the upper limits for concentration should be 32 ml/Liter.

Consumption of the TriCOL BLACK 600 depends on the concentration of TriCOL BLACK 600 maintained in the operating solution. Lower concentrations of TriCOL BLACK 600 such as 1 ml/Liter (0.1%/vol) will require an addition rate of 78 ml /1000 AH(2.6 fl.oz/1000 AH). Higher concentration of TriCOL BLACK 600 32 ml/Liter (3.2%/vol) will require an addition rate of 113 ml/1000 AH (3.8 fl.oz/1000AH).



Temperature

The process operates at 27 - 43°C (80 - 110°F), heating will be required. If production is above 0.5 amperes/Liter 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 2.6 and 2.8. Raise the pH 0.1 unit with the addition of 2 ml/Liter (2 gallons/1000 gallons) ammonium hydroxide. Lower the pH 0.1 unit with the addition of 2 ml/Liter (2 gallons/1000 gallons) hydrochloric acid. pH adjustments will produce an artificially large change in pH that will equilibrate after a period of time. It is also recommended that pH buffers of 2.0 and 7.0 be used to calibrate the pH meter that will be used for analyzing the solution.

EQUIPMENT

TriCOL Anodes

Graphite anodes from Columbia Chemical must be used. Anode length should be approx. 2.5 - 3.75 cm (1 - 1.5 inches) shorter than the rack package at each end when measured from the top of the top piece on the rack to the bottom of the bottom piece on the rack. The anodes should also be at least 5 cm (2 inches) below the solution level.

Generally twice the area of anode area to cathode area should be used. The maximum current density on the anodes should be 540 amperes/m² (50 amperes/ft²). The graphite anode must be mounted below the surface of the solution. The copper bussing should be plated with a layer of nickel prior to installation; this will minimize the amount of copper contamination. Once the hangers are mounted to the buss bars, the buss bar should be wrapped with waterproof plastic tape or covered with other inert plastic material.

TriCOL Anode Hangers

Anode hangers are available from Columbia Chemical.

Air Agitation

Air agitation should be as mild and uniform as possible. High agitation can result in reduced coverage while low agitation can result in uneven metal distribution. Air must be provided from an oil free blower. Perforated plastic air lines must be installed to give uniform mild agitation below the cathode area.

Ampere-Hour Meter

Product additions to the solution are made by ampere-hours. A suitable ampere-hour meter should be used to ensure proper control of the process. An automatic metering pump for the TriCOL Replenisher300 and the TriCOL Black 600 is usually recommended.

Rectifiers

12 or 15 volt rectifiers are normally recommended however existing 6 - 9 volt rectifiers have been used in some installations. The TriCOL trivalent chromium process will not burn therefore higher voltages are normally used to provide superior covering power when compared to an existing hexavalent process.

TriCOL PURE Ion Exchange Systems

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

TriCOL PURE Ion Exchange Resin

Obtain the special Ion Exchange resin from Columbia Chemical. Consult Columbia Chemical for specific volume recommendations.

TriCOL BlackJack Analysis Procedures

Trivalent Chromium

REAGENTS: 30% Hydrogen Peroxide solution, AR (see Note)
50% Sodium Hydroxide Solution
10%w/volume Potassium iodide solution
1:1 Sulfuric acid solution (Dilute concentrated sulfuric acid 1:1 with DI water, use caution when mixing, always add acid to water.)
1% Starch Indicator solution
0.100 N Sodium Thiosulfate solution

EQUIPMENT: 5 mL Pipet, volumetric
100 mL Volumetric flask
250 mL Erlenmeyer flask

PROCEDURE:

- 1) Pipette 5.0 mL of filtered solution into a 100 mL volumetric flask and dilute to volume.
- 2) Pipette 5.0 mL of the solution from the volumetric flask directly to the Erlenmeyer flask.
- 3) Add 6 drops of 30% Hydrogen Peroxide.
- 4) Add 4 drops of the 50% Sodium Hydroxide solution.
- 5) Swirl lightly and insert into the boiling water bath. Maintain heat for 10 minutes. All traces of gassing should be removed.
- 6) Add 5 mL 10% Potassium Iodide solution and mix.
- 7) Add 10 mL 1:1 Sulfuric acid and immediately titrate with 0.1 N Sodium Thiosulfate solution until the solution turns a light yellow color.
- 8) Add 1 mL of 1% Starch Indicator solution and again titrate to the disappearance of the dark blue starch/iodine color.

Calculate the concentration as follows:

$$\text{oz/gal Cr}^{+3} = \text{mL } 0.1 \text{ N Na}_2\text{S}_2\text{O}_3 \times 0.904$$

$$\text{g/L Cr}^{+3} = \text{oz/gal} \times 7.5$$

Determination of Surface Tension

EQUIPMENT: Stalagmometer: Available from Kocour

PROCEDURE:

The TriCOL Antimist 400 concentration can be determined by checking the surface tension of the solution. The stalagmometer number of drops delivered for a certain volume is determined by the specific gravity, surface tension, and the specific gravity of the solution.

The stalagmometer will supply directions with the instrument that should be followed.

Standards should be made with each stalagmometer using a plating solution that has no TriCOL Antimist 400.

Standards should be made at 0.0, 1.0, 2.0 and 3 ml/Liter of TriCOL Antimist 400 to prepare a concentration versus surface tension graph. Take an average of three readings for each standard.

Calculate surface tension as:

$$\text{Surface Tension (Dynes /cm)} = \frac{\text{SW} \times \text{NW} \times \text{D}}{\text{N} \times \text{DW}}$$

D= Density of the Sample in grams/ml

DW= Density of the water in grams/ml

N= Counted number of drops of the sample

NW= water number engraved on the stalagmometer.

SW= Surface tension of the water (72.0 dynes/cm)

TriCOL Blackjack Solution Control

Overview

TriCOL plating solutions utilize a weak complex to deposit trivalent chromium. Trivalent chromium solution must be properly maintained to provide the correct amount of complexed chromium. Additions should be made frequently to provide consistent concentration of the constituents.

TriCOL BlackJack Addition Agent Consumption

TriCOL plating solutions are consumed by electrolysis and by drag-out. Drag-out affects all the addition agents but electrolysis only affects certain addition agents.

<u>Electrolysis and Drag-out</u>	<u>Drag-out</u>
TriCOL Replenisher 200	TriCOL T-Salts 100
TriCOL Replenisher 300	
TriCOL Antimist 400	
TriCOL Black 600	

Addition agents that are lost by electrolysis can be replaced by ampere-hour determination. Materials that are lost by drag-out can be replaced by checking the specific gravity of the plating bath.

Use the log sheet provided on the following page to determine the appropriate additions to the TriCOL plating solution. High drag-out or low drag-out may require adjustment to the addition rates for the TriCOL process.

HANDLING & STORAGE

TriCOL additives can produce temporary irritation when they come into contact with the skin. Therefore, care should be taken to prevent accidental eye and skin contact. Rubber gloves, a rubber apron, and protective goggles should be worn when handling TriCOL additives. In case of contact, immediately flush with copious amounts of water and scrub well with soap and water. TriCOL additives are stable on standing and have a shelf life in excess of two years.

FREEZABILITY: As with most chemical products, it is preferable that freezing be avoided. However, if freezing should occur during transportation or storage, directions for handling the products covered in this technical data sheet are as follows:

If TriCOL Replenisher 300 freezes, simply allow the container to completely thaw and bring to room temperature of 70° - 75°F/ 21° - 24°C. Thoroughly mix to bring back to original condition.

If TriCOL Antimist 400 freezes, simply allow the container to completely thaw and bring to room temperature of 70° - 75°F/ 21° - 24°C. Thoroughly mix to bring back to original condition.

If TriCOL CD PLUS 500 freezes, simply allow the container to completely thaw and bring to room temperature of 70° - 75°F/ 21° - 24°C. Thoroughly mix to bring back to original condition.

If TriCOL BLACK 600 freezes, simply allow the container to completely thaw and bring to room temperature of 70° - 75°F/ 21° - 24°C. Thoroughly mix to bring back to original condition.

NON-WARRANTY

The data contained in this bulletin is believed by Columbia Chemical Corp. to be accurate, true and complete. Since however, final methods of use of these products are in the hands of the customer and beyond our control, we cannot guarantee that the customer will obtain the results described in this bulletin, nor can we assume any responsibility for the use of this product by the customer in any process which may infringe the patents of third parties.