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Pilot Line Testing of a New, High-Speed Sulfate-Based Tinplate Process

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Metal Bulletin

TIN TECHNOLOGY
FOR A CLEANER FUTURE

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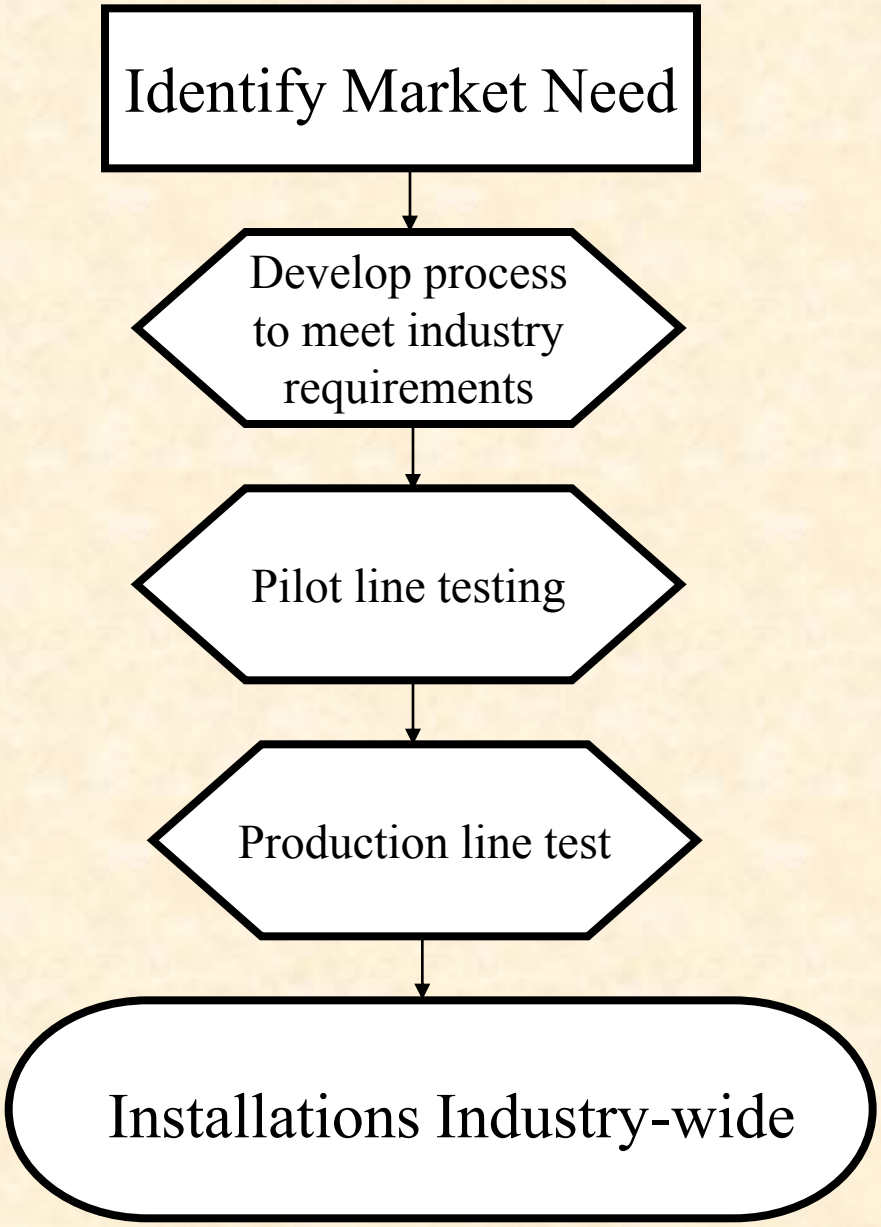
Technistan TP Process Development Chart



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Tinplate Industry Needs

- Lower cost tinplate process.
- Reduced environmental burden.
- Increased operating windows.

Development of the Process
Presented in 2004

- Process components:
  - Tin Sulfate: 20 g/l Sn^{+2}
  - H_2SO_4: 50 ml/l
  - Technistan TP Additive: 50 ml/l
  - Technistan Antioxidant: 20 ml/l
- Current Density Range (CDR) Testing:
  - Hull Cell: 0 – 12 a/dm^2
  - Rotating Cathode @ 80 mpm: 10 – 40 a/dm^2
- Deposit Uniformity on CDR Test Vehicles:
  - Visually uniform deposit under both forms of CDR testing
  - Uniform deposit morphology @ 2000X by SEM analysis

Development of the Process
Presented in 2004

- Fe^{+2} Contamination Effects:
  - No effect on current density range
  - No effect on Sn^{+4} generation rate
- Sn^{+4} Generation Rate in a Nippon Steel Tin Dissolution System Pilot Line:
  - 4% of anode weight with 20 g/l Fe^{+2}
  - 14% and 18% rates with MSA and PSA, respectively
- Cathode Efficiency:
  - 95+% under tinplate current density range
- Cost:
  - Projected to be **at least 30% lower** than MSA processes.

Pilot Line Testing
2004 to Present

- Tinplate Industry Pilot Lines:
  - Flow Cell/Rotating Cathode Machines
  - 30-40 meter plating lines with in-line reflow furnaces
    - Very few in number
    - Operate at relatively low line speeds: 10 –100 mpm
  - Limited amount of actual plating time, so the plating bath is not tested for durability.
- Alternative "Pilot" Lines:
  - Copper Wire Tinning Lines
  - Copper Strip Tinning Lines with In-line Reflow
  - ➢ **These lines are production lines, and solution durability is absolutely critical.**

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Neumann High Speed (900 mpm) Wire Line

Wire Line Operating Parameters

Operating Parameter	Range	
Plating Process	Sulfate Based	MSA Based
Sn^{+2}	15 – 50 g/l	50 – 100 g/l
Acid	30 – 70 ml/l	50 – 150 ml/l
Additive	30 – 80 ml/l	50 – 150 ml/l
Antioxidant	10 – 30 ml/l	10 – 30 ml/l
Temperature	35 - 55ºC	35 - 55ºC
Cathode Efficiency	95% or higher	95% or higher
Line Conditions		
Line Speed	200 – 1200 mpm	
Rectifier Amperage	4000 – 10,000	
Current Density	10 – 80 a/dm^2	
Plating Thickness	20 – 100 g/m^2	

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Wire Line
Similarities/Differences

- Similarities to a Tinplate Line
  - Line speeds and current densities
  - Tin concentration for sulfate based process
  - Use of insoluble balancing anodes
  - Concern about tin sludge and tin dust
  - Concern about tin deposit morphology
  - Concern about process “running cost”
- Differences from a Tinplate Line
  - Deposit thickness
  - No reflow requirement
  - Deposit visual uniformity is not important

Wire Line History

Technistan TP

- 20+ wire lines are now running with the tin sulfate process. Oldest installation is from December 2004.
- Tin deposit is "brighter" than competitors' baths running MSA processes at all production current densities.
- At least 50% reduction in Sn^{+4} generation compared to MSA processes: ≤ 0.5% of the installed tin anode weight
- 35 – 40% reduction in "running costs" for the chemical components. Not factored in is cost reduction in tin drag-out.
- No wire customer has gone back to operating his former process after converting to the Technistan TP process.

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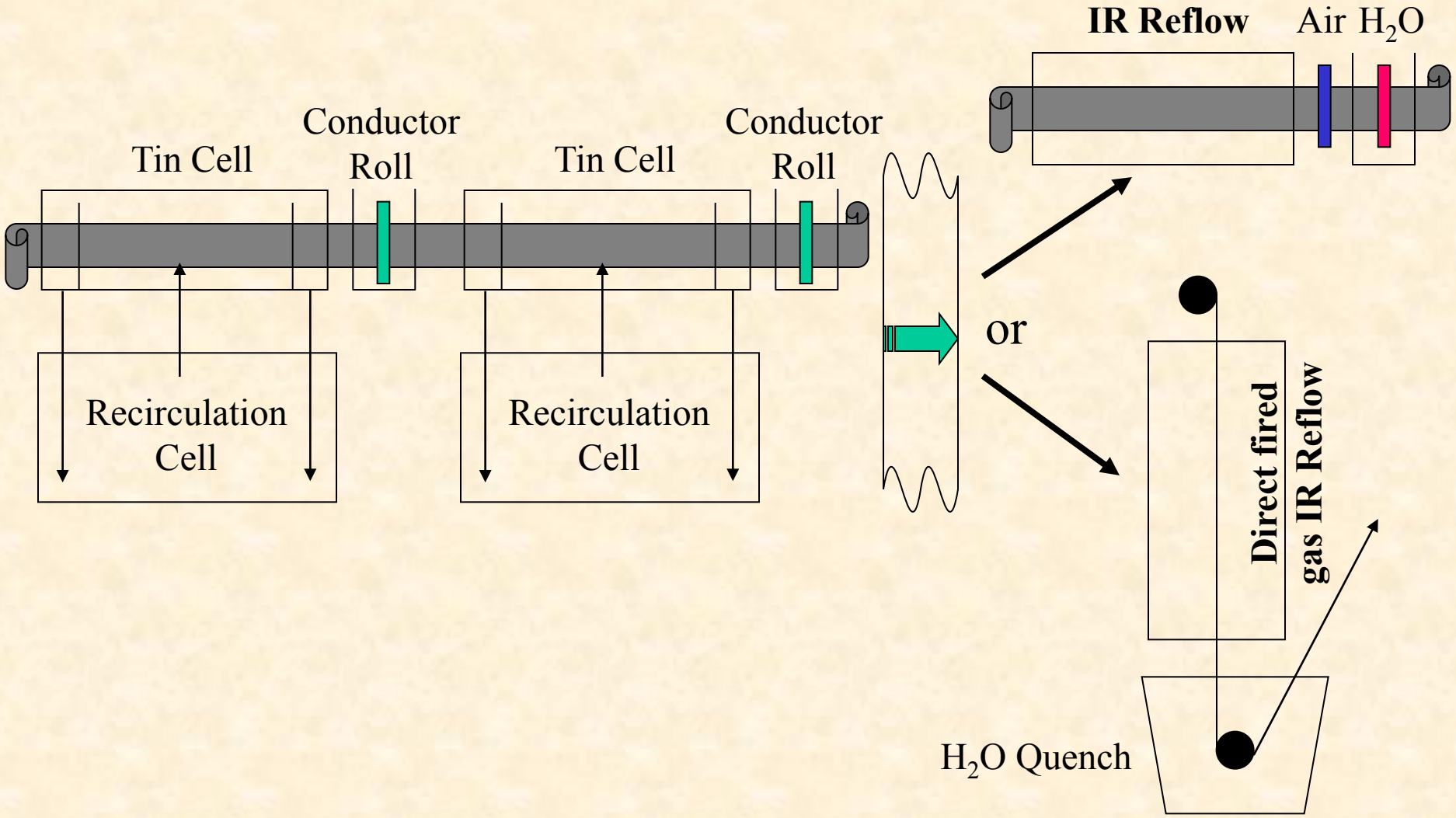
Copper Strip Plating Lines

- Standard plating line layout (rinses omitted):
  Clean ➔ Pickle ➔ Tinplate ➔ Neutralize ➔ Flux ➔ Reflow ➔ Quench ➔ Dry ➔ Recoil
- Product is used for automotive connector stock.
- Multiple tin plating tanks are used. Lines are usually 40 to 50 meters long.
- Reflow is by IR lamps (strip in horizontal position) or by direct gas fired IR (strip in vertical position). IR lamps use a combination air/water quench. Direct gas fired IR reflow lines use a standard water quench.

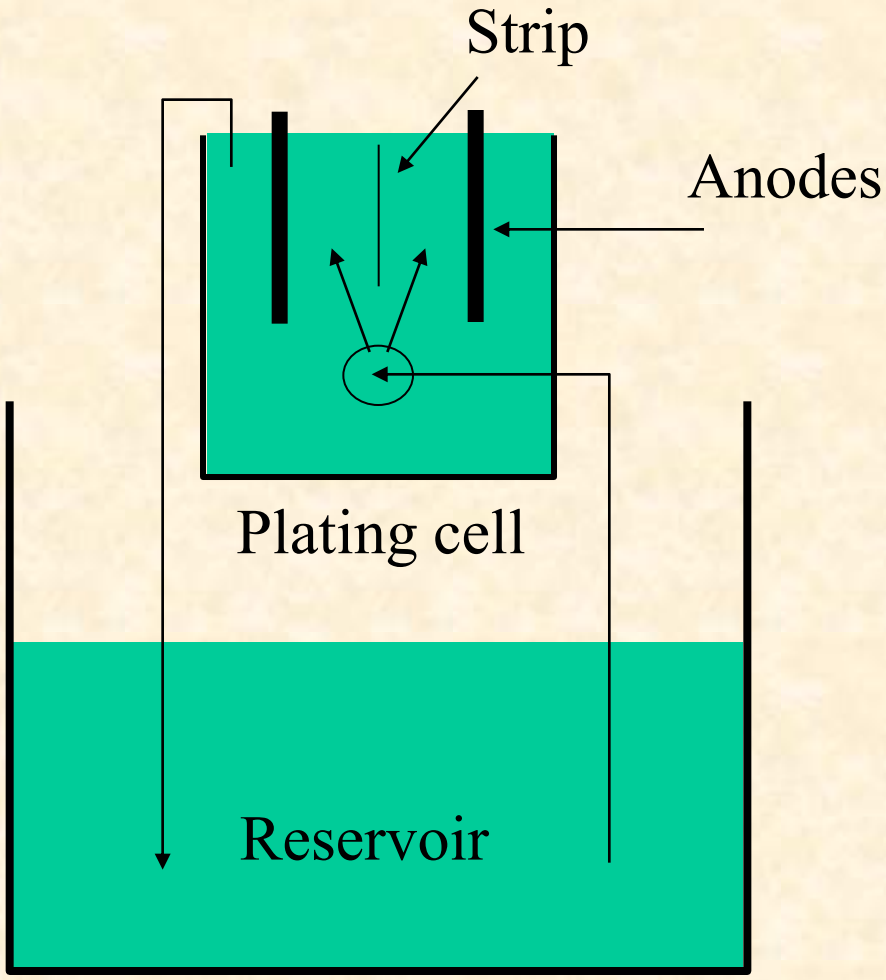
Copper Strip Line Schematic

Side View:Tin & Reflow Sections



Schematic of Copper Strip Line Cell

End View



Copper Strip Line Operating Parameters

Operating Parameter	Range
Plating Process	Sulfate Based
Sn^{+2}	20 – 35g/l
Acid	30 – 70 ml/l
Additive	30 – 80 ml/l
Antioxidant	10 – 30 ml/l
Flux (Cl^- based)	0.5 – 1.5% v/v
Temperature	35 - 50ºC
Cathode Efficiency	95% or higher
Line Conditions	
Strip Width	10 – 400 mm
Line Speed	15 – 30 mpm
Rectifier Amperage	300 - 600
Current Density	4 – 10 a/dm^2
Plating Thickness	5.8 – 18 g/m^2

Copper Strip Line
Similarities/Differences

- Similarities:
  - Tin concentrations
  - Strip is sufficiently wide to see current density effects
  - Coating weights
  - Type of flux used
  - **Reflowed deposit**
- Differences
  - Line speeds
  - Current Densities
  - No woodgrain is possible
  - No contamination of Fe in the electrolyte

Copper Strip Line History

- 4 lines installed, with the oldest operating 16 months. 5th line to be installed in October 2006.
- Uniform, mirror bright deposits after reflow. Uniform matte deposit appearance before reflow.
- Additive stability is excellent: 3X less consumption than 2 competitors.
- Analysis of the Additive is by surface tension. Easy to maintain proper bath conditions.
- No reason why the substrate must be copper based. Steel substrates have been run on these lines in the past, and therefore, a trial run of blackplate with the tin sulfate process was arranged with a US tinplate producer.

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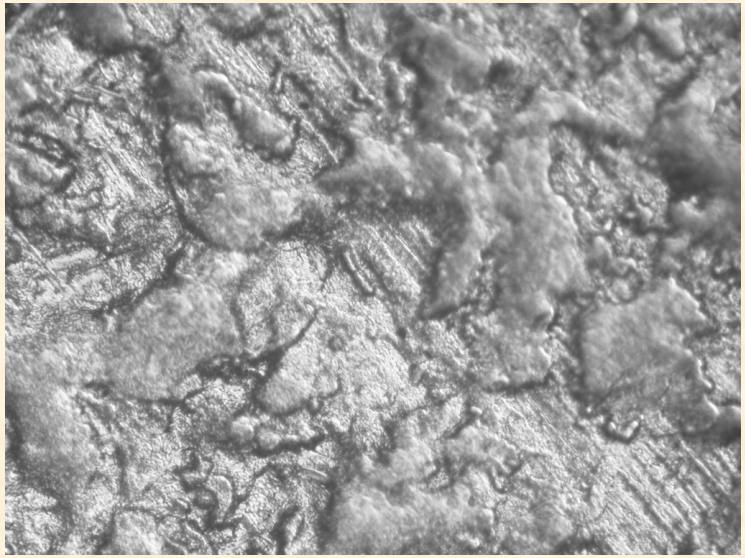
Blackplate/Tinplate Trial

- 2 commercial blackplate coils were slit to 254 mm width and 1 tonne weights:
  - Coil 1: 0.33 mm thick with a blast finish
  - Coil 2: 0.21 mm thick with a Grade C finish
- Production Plan:
  - Coil 1: plate matte deposits at 2.8, 5.6, and 8.4 g/m2. Deposit was left in the matte state to evaluate coating uniformity.
  - Coil 2: plate and reflow 2.8 g/m2 deposits. Reflow was the direct gas fired IR with a water quench.
  - Send both coils back to US tinplate producer for evaluation

Blackplate/Tinplate Trial
Details

- Coil 1
  - Line Speed: 11.6 mpm
  - Current Density: 3.6 a/dm^2
    - 3 cells used for 8.4 g/m^2
    - 2 cells used for 5.6 g/m^2
    - 1 cell used for 2.8 g/m^2



2.8 g/m^2 @ 400X

  - **Tin deposit was uniform in appearance across the web.**

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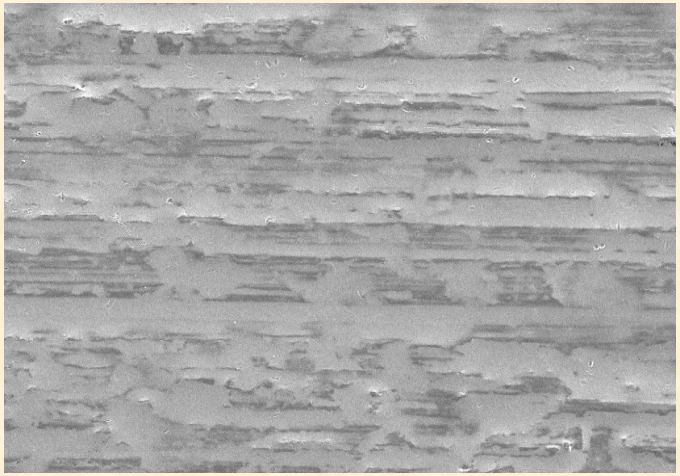
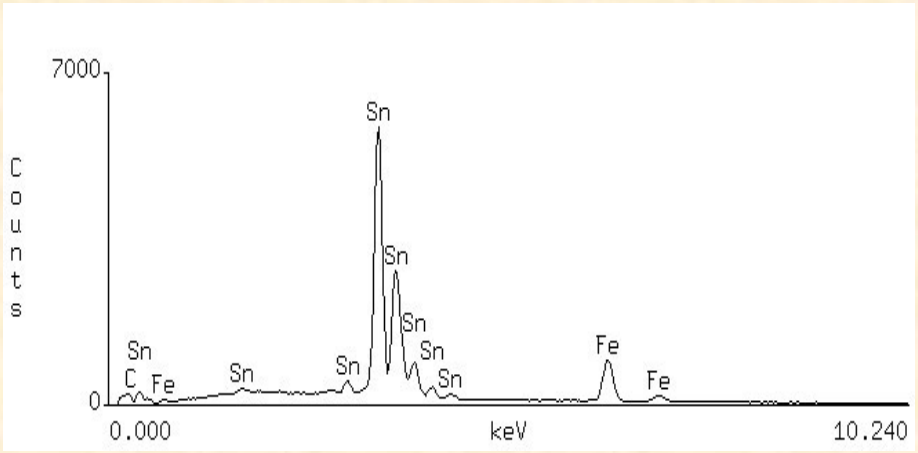
Blackplate/Tinplate Trial
Details

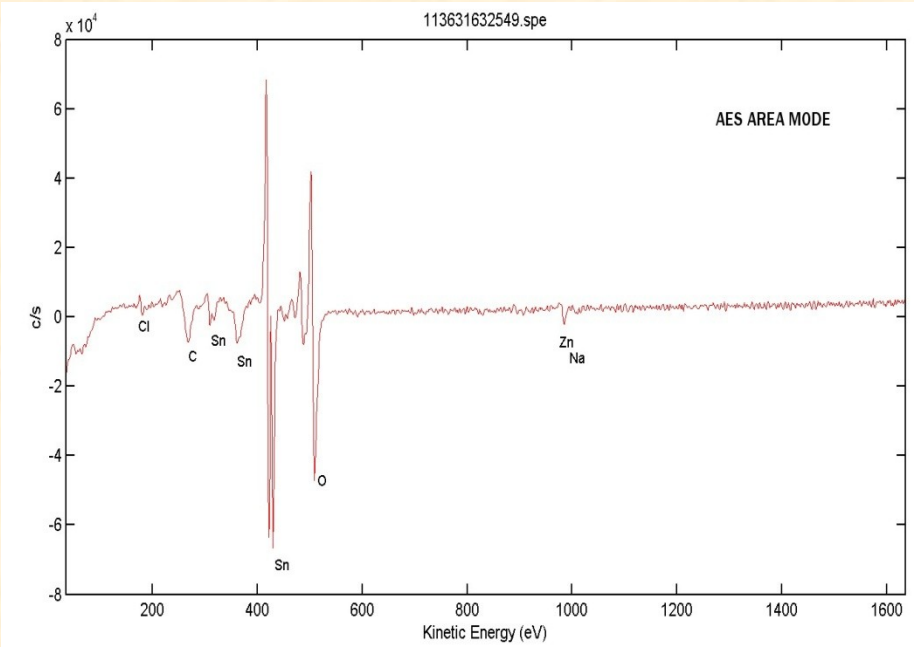
- Coil 2
  - Line Speed: 16 mpm
  - Current Density: 6 a/dm^2
  - Only one plating cell was used.
  - **Reflowed strip had a uniform, bright appearance that looked identical to commercial 2.8 g/m^2 tinplate.**
- Both coils were sent back to the tinplate producer for further evaluation: SEM, EDX, Auger, and ESCA.



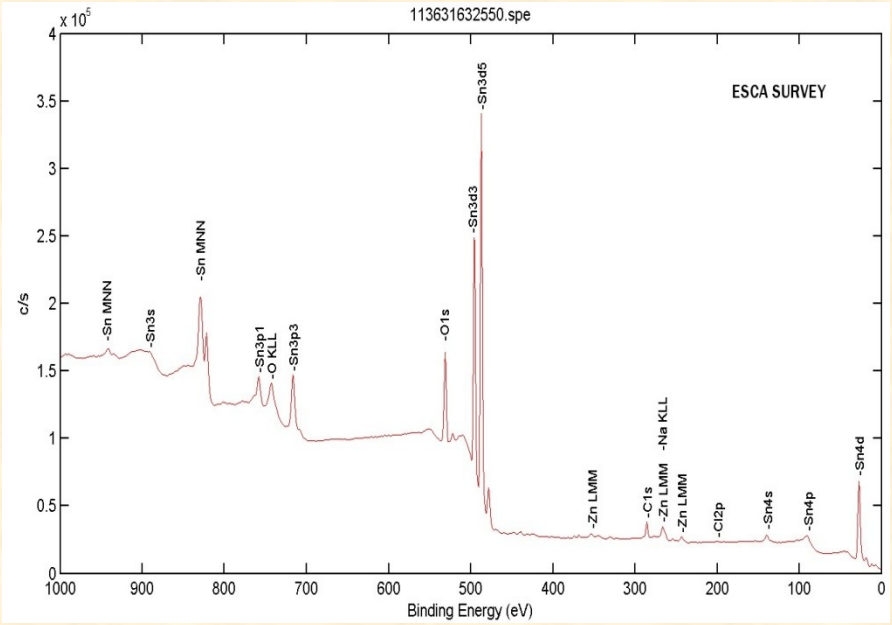
250X SEM



EDS Spectra



Auger



ESCA Spectra

High Speed Flow Cell Pilot Line

- US Tinplate Producer's High Speed Flow Cell:
  - Simulates line speeds from 30 mpm to 950 mpm
  - Rectification runs by coulomb set, eliminating false current densities because of rectifier ramping.
  - Test panels are cut from commercial blackplate and are 133 mm long by 55 mm wide
- Conduction Reflow Unit
  - After plating, the panels are connected to a conduction reflow unit with an integrated water quench.
- Target Plating Thickness: 2.8 g/m^2

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Flow Cell Chemistry

Operating Parameters	Bath 1	Bath 2
Sn^{+2}	20 g/l	
Fe^{+2}	0	20 g/l
H_2SO_4	50 ml/l	
Additive	50 ml/l	
Antioxidant	50 ml/l	
Temperature	50 C	

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Test Matrix

Line Speed (mpm)	Current Density (a/dm^2)			
	10	30	50	90
100	X	X		
160	X	X	X	
300	X	X	X	
420		X	X	
485		X	X	X

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Flow Cell Pilot Line Test Results

- Panels plated at all current densities and line speeds show a uniform appearance, with virtually no color change.
- Iron contaminated bath performed the same as the non-contaminated bath. No difference in current density performance or coating appearance.
- No burning (dendritic deposit morphology) was observed on any of the panels, including the panels plated at 90 a/dm2.
- Reflowed panels were bright and uniform in appearance. NO WOODGRAIN, even though the panels were not fluxed.

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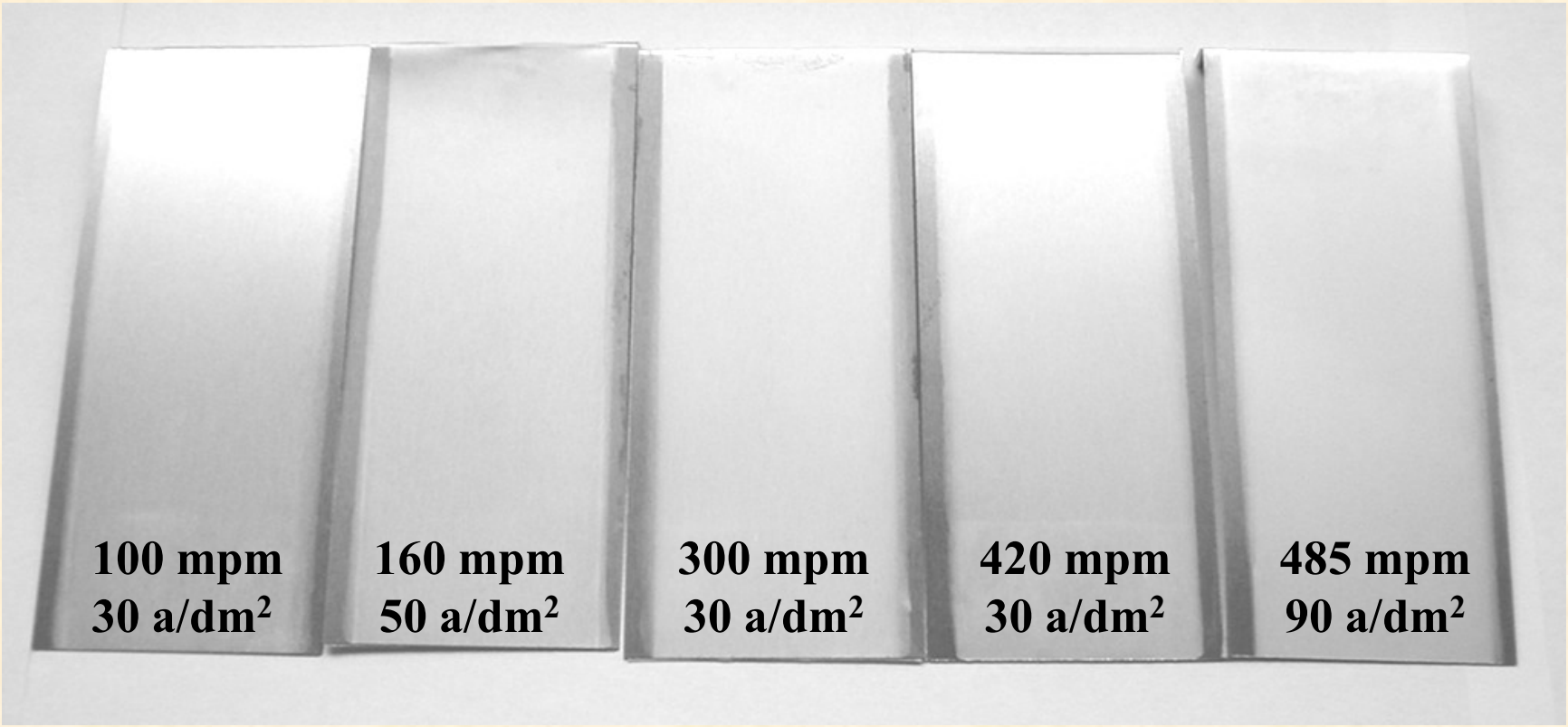
Representative Panels from Flow Cell Test



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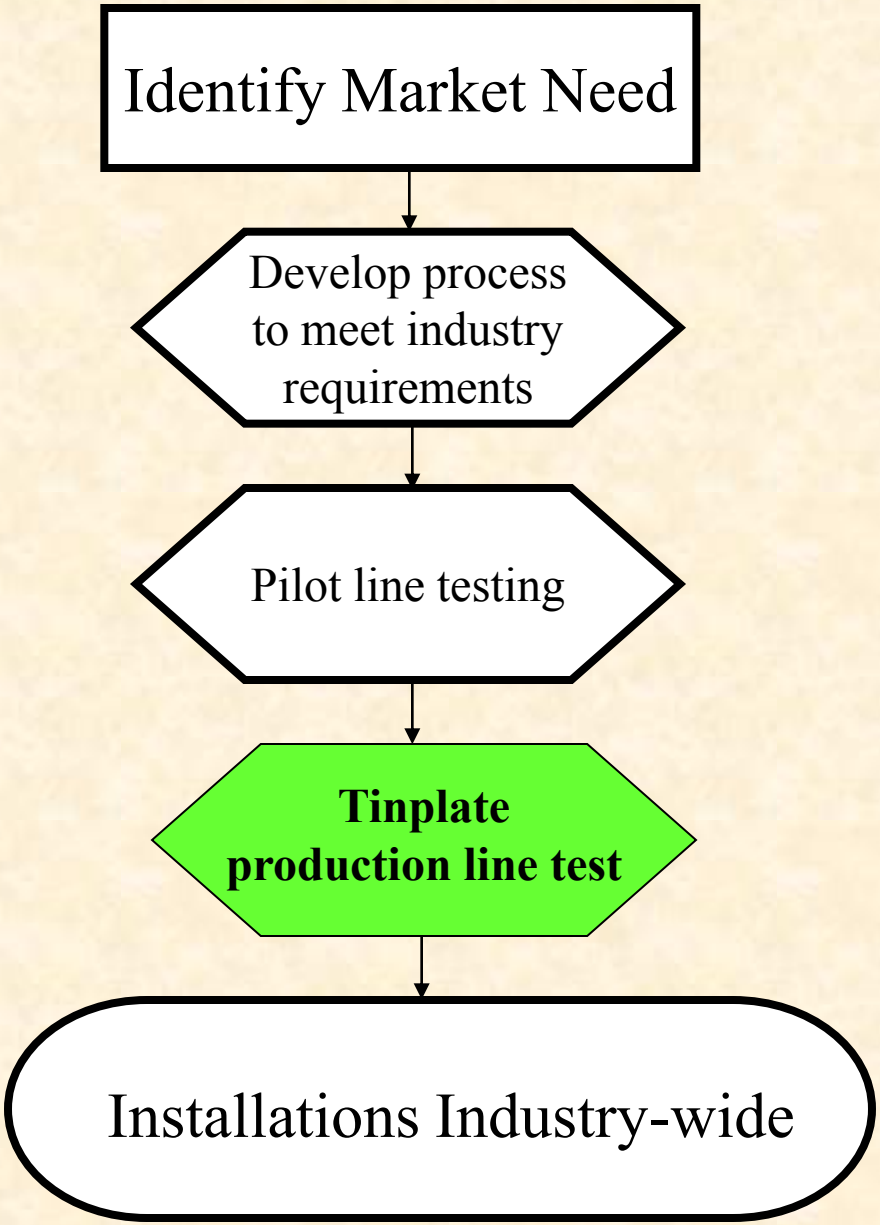
10 a/dm^2 Effect

- Panels plated at 10 a/dm^2 showed approximately 50% cathode efficiency (1.4 g/m^2 coating weights). Cathode efficiencies at all other current densities were close to 100%.
- Production experience on the copper strip lines show cathode efficiencies at 5 to 10 a/dm^2 are close to 100%. Plating has also been done at this current density on wire lines with no loss in cathode efficiency.
- We believe the problem lies with the increased conductivity of the tin sulfate bath. The bath is approximately 30% more conductive than an MSA process, and 50% more conductive than a PSA process. The high conductivity results in very low voltage at the 10 a/dm^2 condition in the flow cell. The voltage is so low that tin overvoltage (voltage that must be reached before tin plating occurs) is a significant fraction of the system voltage.

Conclusion

- The Technistan TP process is a production proven process in the wire and copper strip plating industry. The lines used in these industries can be considered “pilot lines” by the tinplate industry.
- The Technistan TP process has been proven superior to other processes by the wire and copper strip industries for:
  - Process durability
  - Uniformity of visual appearance across the usable current density range for both matte and reflowed finishes
  - Reduced stannic tin generation
- Flow cell pilot line testing shows the process has an exceptionally wide current density range with a uniform deposit appearance. Iron has no effect on the process.

Technistan TP Process Development Chart



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