Analysis of Multi-component Dye Baths Using CIELAB and Reflectance Spectrophotometry

1) Overview
    a) Competitive finishes and substitute materials pose a challenge to the anodize industry
        i) Wet and powder paints afford:
            (1) Almost infinite color palette choices
            (2) Greater color consistency
        ii) Substitute materials: polymers and plastics
            (1) Similar advantages of wet and powder paints
            (2) Advancements in materials are penetrating traditional anodize markets
                (a) Example: poured polymer lowers in the firearms industry for modern sporting rifles
    b) Market advantages of anodized aluminum
        i) Designers like the look and feel of anodized aluminum
            (1) Competitive finishes and substitute materials cannot match the metallic look of anodized aluminum (yet)
            (2) Anodize aluminum projects quality and value to the consumer
        ii) Designers want color options
            (1) Projects are often lost because a specific color cannot be achieved
        iii) Project seeks to develop methods to control production dye baths to achieve:
            (1) Additional color options through complex dye blends
            (2) Increased color uniformity through dye bath control
            (3) Maintain existing market shares and develop new market shares
    c) Current state of anodized dye bath controls
        i) Multi-component organic dye baths are difficult to control
            (1) Disproportionate consumption shifts color
            (2) Disproportionate vulnerability towards contaminants shifts color
            (3) Decreased dye activity over time shifts color
        ii) Need to develop a control method to adjust dye baths prior to color shifts
            (1) Transmission of dye baths was tested
                (a) Sample of dye bath analyzed using UV-Vis spectrophotometry
                    (i) Various dye concentrations determined
                (b) Abandoned as results did not always correlate with actual physical dyeing
        iii) Reflectance values of physical dyeings
            (1) Direct correlation to the bath performance
            (2) More accurate and detailed reading of color deviation than the human eye can detect
                (a) Enables bath adjustment prior to color variation rejection.
2) Background on Color Theory
    a) Terms
        i) Lightness: How bright or dark a color is
        ii) Hue: Where a color falls on the color wheel
        iii) Saturation: How vivid or dull a color is
    b) Color wheel
        i) Very important to understand and reference

ii) Defines “opposite” color
(1) Helps select the dye to neutralize a negative color progression
c) Color Spaces
i) Method of expression color of an object or light source using some kind of notation (numbers)
(1) L*a*b or CIELAB
(a) L: ranges from 0 (white) to 100 (black)
(b) a*: ranges from negative (green) to positive (red)
(c) b*: ranges from negative (blue) to positive (yellow)
(2) L*C*h color space
(a) L*: ranges from 0 (white) to 100 (black)
(b) C*: chroma
(c) h*: hue
d) Wavelength and Reflectance
i) Color: human eye’s perception of reflected radiation in the “visible” spectrum of electromagnetic radiation
(1) 400 (purple blue) to 700 nm (red)
(2) Think rainbow!
3) Experiments
a) Green AEN
i) Color shifts between blue green and yellow green
ii) Two component dye (Blue and Yellow)
iii) Baths were made using:
(1) Standard concentrations
(2) High blue component concentration
(3) High yellow component concentration
iv) Analysis of dyeings performed using reflectance spectroscopy
(1) Graphs of the three readouts show distinct shifts
v) Bath exhaustion
(1) Total DE of 8
(a) Most came from DL at 7.8
(2) Added 25% replenishment
(a) Readings improved to under tolerances (DE <4)
vi) Contamination
(1) 1000 ppm sulfate added to affect color
(a) Shifted color to blue
(i) Yellow component adversely affected compared to the blue component
(b) Shifted L value
(i) Overall decrease in both component’s activity
(c) Added yellow component and standard blend
(i) Recovered bath performance
vii) Production bath
(1) DE 6.67 from standard
(a) Da 4.38 (more red) and Db 4.57 (more yellow than standard)

        - (b) Dye not green enough
      - (2) Added blue and green
        - (a) DE 3.85
          - (i) Da 3.82
        - (b) Recovered bath performance DE <4
          - (i) Inability to adequately change the Da is a warning marker for life of the bath
            - 1. Helpful for total process control
- b) Coyote Brown (custom color MIL SPEC)
  - i) 2 component dye: Bronze 2LW (40%) and Grey HLN (60%)
    - (1) More complex reflectance data than Green AEN (multiple peaks)
    - (2) Higher grey and higher bronze ratios create different data profiles
  - ii) Contamination
    - (1) Added 1000 ppm sulfates
    - (2) Significantly lighter color
    - (3) Made subsequent adds to the dye bath
      - (a) At 110%, bath was recovered
      - (b) At this level of recovery, a new bath would be preferred
        - (i) Actual production would not see a sudden 1000 ppm sulfate contamination
        - (ii) Steady increase in dye concentrations would combat contamination
          - 1. Maintain color consistency
          - 2. Maintain production
  - iii) Test: Random bath make-up
    - (1) Colleague made a 2 g/L bath with a random concentration of the two components
      - (a) Can the bath be adjusted back to standard?
    - (2) Deviation of random bath from standard
      - (a) DE: 11.24
      - (b) Da: -5.97
      - (c) Db: -9.5
      - (d) DL: .72
      - (e) Color looks less red and more blue
    - (3) Made dilution of bath and added 40% Bronze 2LW
      - (a) Results
        - (i) DE 2.33 (success DE<4)
        - (ii) DL: -.48
        - (iii) Da: 1.46
        - (iv) Db: -1.27
- c) Black MLW (3 component black at 2 g/L)
  - i) Bath Exhaustion
    - (1) DE: 7.52
      - (a) DL 7.24
        - (i) Dye consumption most affecting color change
      - (b) Db -1.92
        - (i) Red and orange component are consumed at a higher rate
      - (c) Correction

- (i) Added 40% MLW back
  - 1. DE 4.09
  - 2. Db -3.84
    - a. Bath became even bluer!
  - 3. Added more orange and brown
    - a. DE 2.6, Db -1
    - b. Success DE < 4
- ii) Contamination
  - (1) 100 ppm aluminum
    - (a) DL 7.24
    - (b) Db -1.92
      - (i) More blue
      - (ii) Brown and orange more adversely affected by contamination
    - (c) Add
      - (i) 1% orange and brown
        - 1. Became too yellow
      - (ii) Added MLW mix
        - 1. DE 0.97 (success DE <<4)
        - 2. Da .96
- iii) Customer Bath (diluted to 2 g/L)
  - (1) Deviation from standard
    - (a) DE 9.70
    - (b) DL -5.25
    - (c) Db -7.93
  - (2) Adjustments
    - (a) 10% dilution
    - (b) Added 1% of brown and orange
  - (3) Results
    - (a) DE 0.45 (success DE<<4)
    - (b) DL 0.51
    - (c) Da -0.95
    - (d) Db .6

d) Production Line

- i) High end marine product: Grey HLN
- ii) Initial concern based on customer's prior experience was shift to red
- iii) Actual problem was shifting to blue
- iv) Customer monitors color output using a spectrophotometer
  - (1) Plots color progression
  - (2) Makes adds of yellow to combat blue progression
- v) Happy end user with production material!