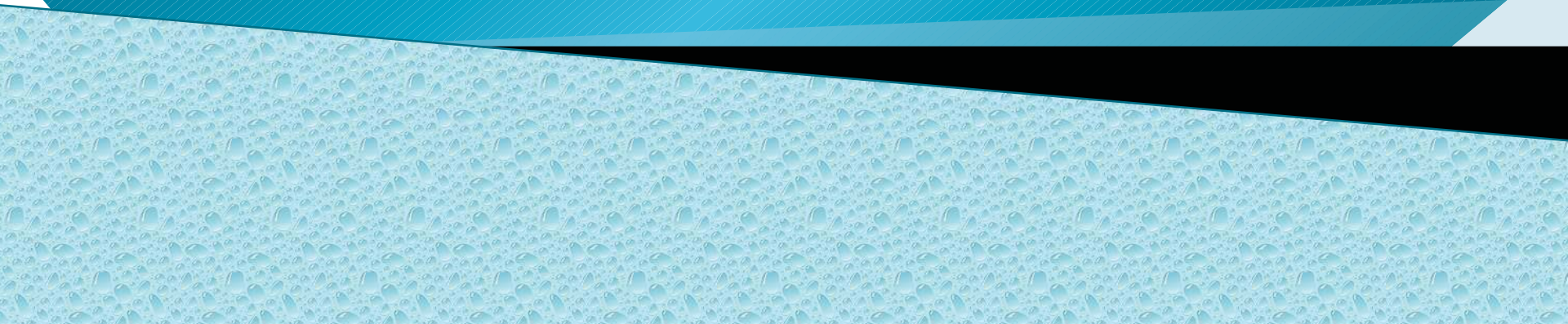


# Fluoroalkyl Silicones in Coatings Films

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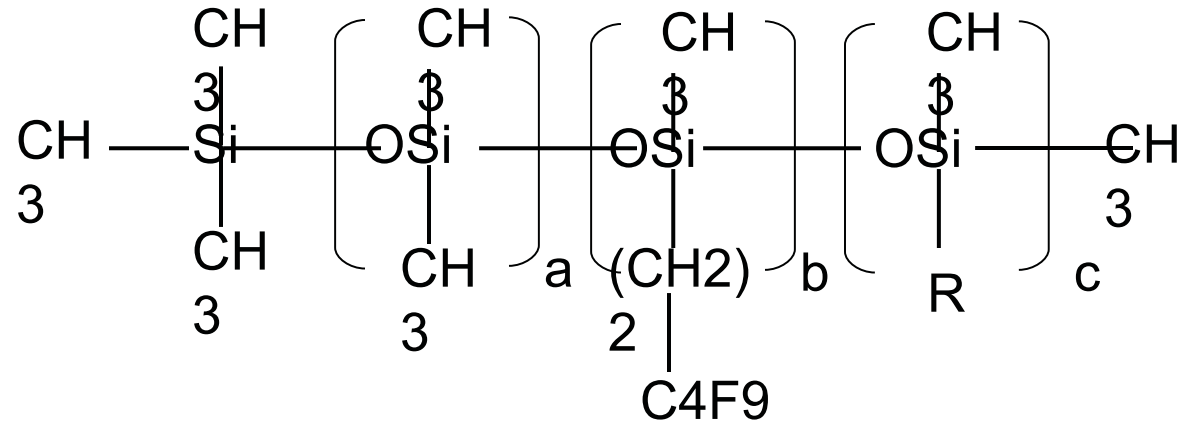


# Experimental and Methodology:

- ▶ The overall design is to use five systems:
  - SB Urethane
  - Urethane acrylate
  - Epoxy acrylate
  - Cationic UV cured epoxy silicone
  - Commercial Paint
- ▶ Various fluoroalkyl silicones are evaluated for slip, COF, defects and mar, stain, and fingerprint resistance.



# Silicone Variations



|     | C  | R                                                                                                                                   |
|-----|----|-------------------------------------------------------------------------------------------------------------------------------------|
| FPE | >0 | (CH <sub>2</sub> ) <sub>3</sub> (OC <sub>2</sub> H <sub>4</sub> ) <sub>d</sub> (OC <sub>3</sub> H <sub>6</sub> ) <sub>e</sub><br>OH |
| FS  | 0  |                                                                                                                                     |
| FA  | >0 | C <sub>n</sub> H <sub>(2n)</sub> R'                                                                                                 |



# Structural Details

|         | Wt %<br>Silicone | Wt %<br>CF2 | Wt %<br>organic | Reac<br>tive<br>Site | Wat<br>er<br>Mis<br>cibl<br>e | MW    | Type                                 |
|---------|------------------|-------------|-----------------|----------------------|-------------------------------|-------|--------------------------------------|
| FPE 1   | 38%              | 8%          | 54%             | OH                   | 1%                            | 3000  | fluoroalkyl<br>polyether<br>silicone |
| FPE 2   | 33%              | 3%          | 64%             | OH                   | 10%                           | 7000  |                                      |
| FS 1    | 56%              | 44%         | 0%              | no                   | no                            | 2000  | fluoroalkyl<br>silicone              |
| FS 2    | 86%              | 14%         | 0%              | no                   | no                            | 14000 |                                      |
| FA 1    | 57%              | 41%         | 2%              | OH                   | no                            | 3000  | alkyl,<br>fluoroalkyl<br>silicone    |
| FA 2    | 68%              | 30%         | 2%              | OH                   | no                            | 3000  |                                      |
| FA 3    | 81%              | 17%         | 2%              | OH                   | no                            | 2000  |                                      |
| FA 3ACR | 81%              | 17%         | 2%              | ACR                  | no                            | 2000  |                                      |
|         | 62%              | 16%         | 21%             |                      |                               | 5000  |                                      |

# Film Properties: SB Urethane

|         | Static<br>COF | Kinetic<br>COF | Gloss | %Gloss<br>Retained | Mar<br>Resist | Surface<br>appearance |
|---------|---------------|----------------|-------|--------------------|---------------|-----------------------|
| Control | 1.397         | 1.500          | 127   | 77.2%              | 1.1           | Smooth                |
| FA 1    | 1.274         | 1.204          | 120   | 95.0%              | 6.4           | Fisheyes              |
| FA 2    | 0.940         | 1.115          | 123   | 86.2%              | 4.3           | Smooth                |
| FA 3    | 0.794         | 0.756          | 113   | 87.1%              | 4.3           | Smooth                |
| FA 3ACR | 0.405         | 0.422          | 107   | 93.1%              | 6.4           | Fisheyes              |
| FPE 1   | 0.577         | 0.631          | 130   | 96.7%              | 6.4           | Smooth                |
| FPE 2   | 0.681         | 0.711          | 128   | 96.4%              | 6.4           | Smooth                |



# Film Properties: UV Ureth. Acryl.

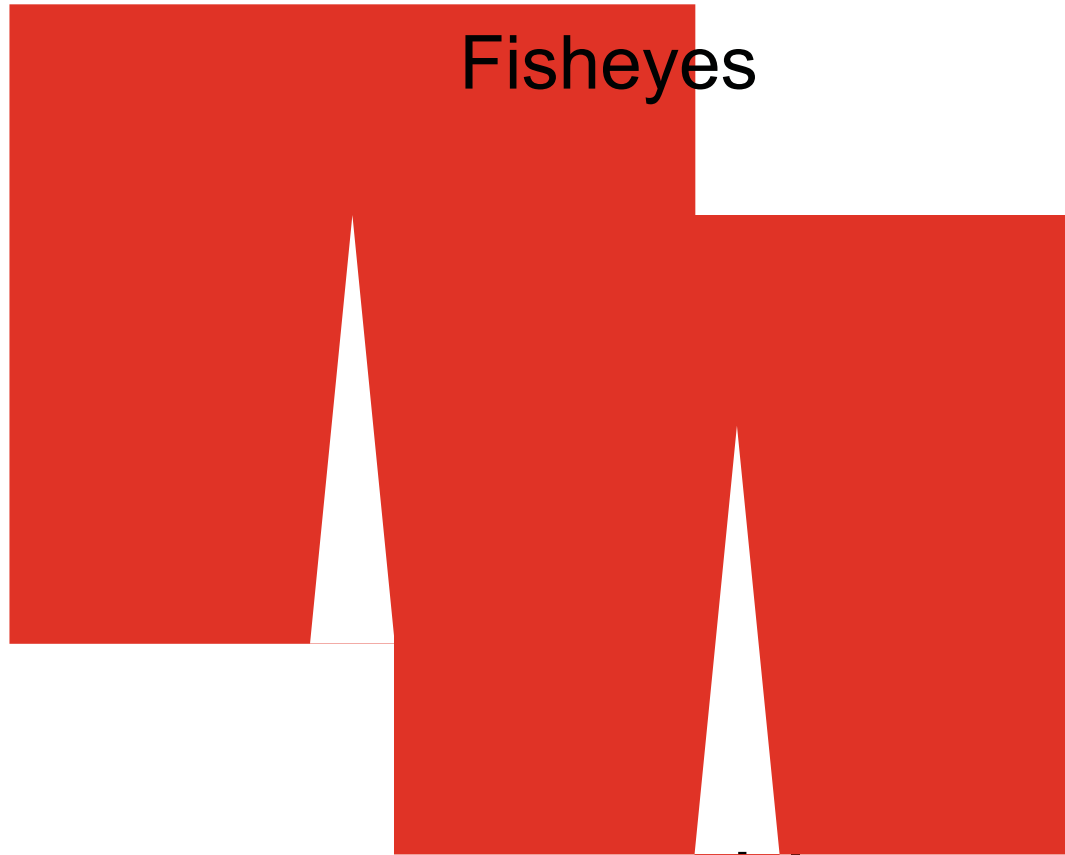
|         | 60°<br>Gloss | Stain<br>Resist | Mar<br>Resist | Static<br>COF | Kinetic<br>COF | Finger<br>Print<br>Resist | Surface<br>Appearance |
|---------|--------------|-----------------|---------------|---------------|----------------|---------------------------|-----------------------|
| Control | 93.2         | 1.7             | 1.0           | 1.99          | 2.18           | 0.5                       | Some<br>craters       |
| FS 1    | 54.6         | 4.0             | 6.0           | 0.93          | 0.93           | 4.5                       | Patches               |
| FS 2    | 76.5         | 6.7             | 5.8           | 1.37          | 1.26           | 6.0                       | Patches               |
| FPE 1   | 92.4         | 7.6             | 5.9           | 1.25          | 1.56           | 2.0                       | Smooth                |
| FPE 2   | 92.9         | 7.6             | 6.8           | 1.31          | 1.34           | 2.0                       | Smooth                |
| FA 3ACR | 68.3         | 8.3             | 8.2           | 0.58          | 0.56           | 5.5                       | Smooth                |
| FA 4    | 79.5         | 5.0             | 7.2           | 0.78          | 0.76           | 5.0                       | Wavy                  |



# Film Properties: UV Epoxy Acrylate

|         | 60°<br>Gloss | Stain<br>Resist<br>ance | Mar<br>Resist<br>ance | Static<br>COF | Kineti<br>c COF | Finger<br>Print<br>Resist<br>ance | Appeara<br>nce |
|---------|--------------|-------------------------|-----------------------|---------------|-----------------|-----------------------------------|----------------|
| Control | 89.0         | 0.5                     | 0.5                   | 2.78          | 2.80            | 0.5                               | Pinholes       |
| FS 1    | 85.5         | 4.2                     | 3.5                   | 2.32          | 2.06            | 5.5                               | Patches        |
| FA 4    | 91.2         | 5.0                     | 3.1                   | 1.88          | 1.80            | 6.5                               | Matte          |
| FS 2    | 90.8         | 6.7                     | 3.8                   | 1.96          | 1.61            | 6.0                               | Patches        |
| FPE 1   | 92.7         | 7.6                     | 4.8                   | 2.08          | 2.33            | 3.5                               | Smooth         |
| FPE 2   | 92.7         | 7.6                     | 6.0                   | 2.26          | 2.76            | 4.0                               | Smooth         |
| FA 3ACR | 88.3         | 8.3                     | 8.5                   | 0.52          | 0.51            | 7.0                               | Smooth         |

# Gloss: SB Urethane

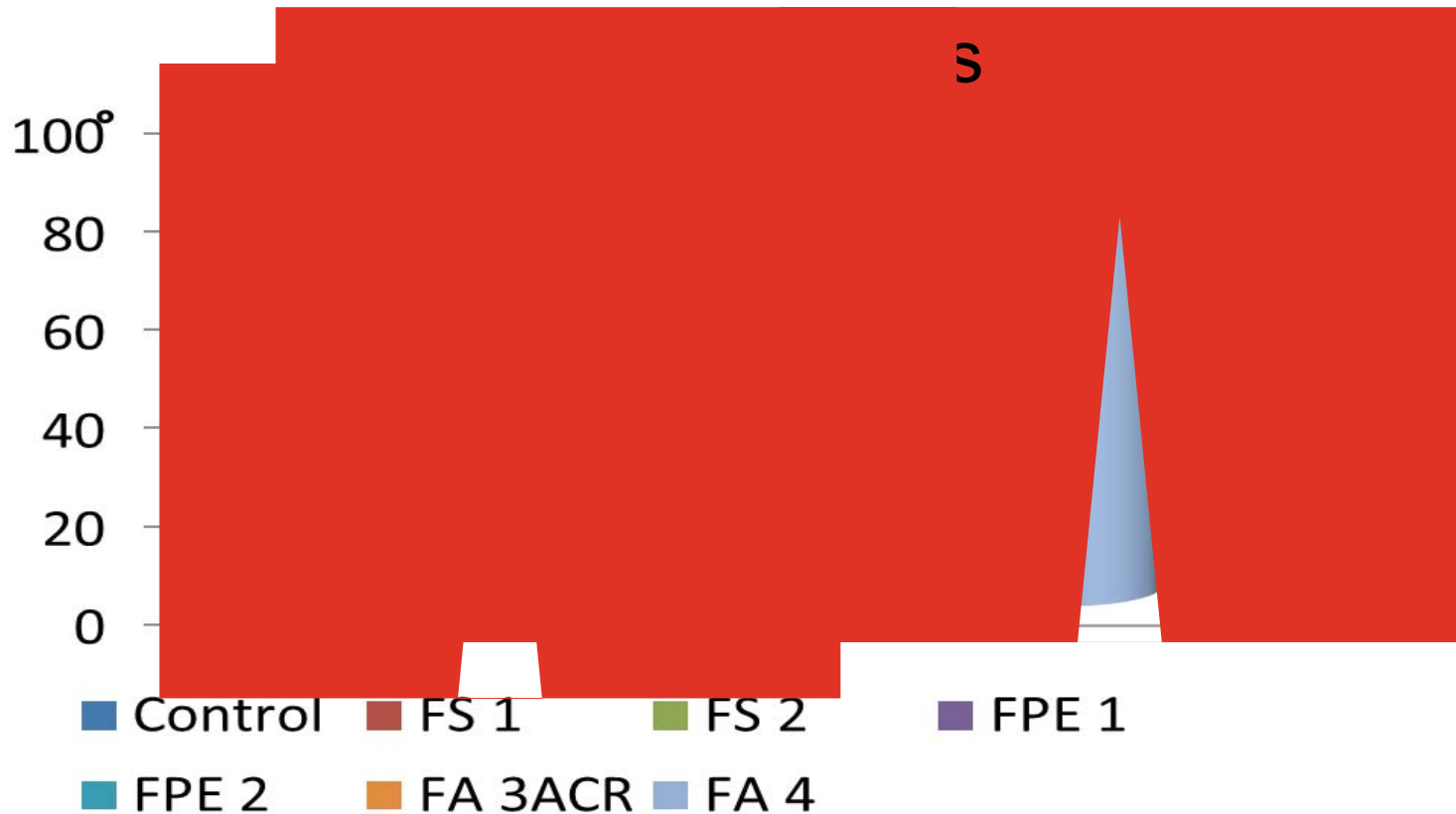


- FPE are most miscible, improve gloss
- FA type decrease gloss cause defects



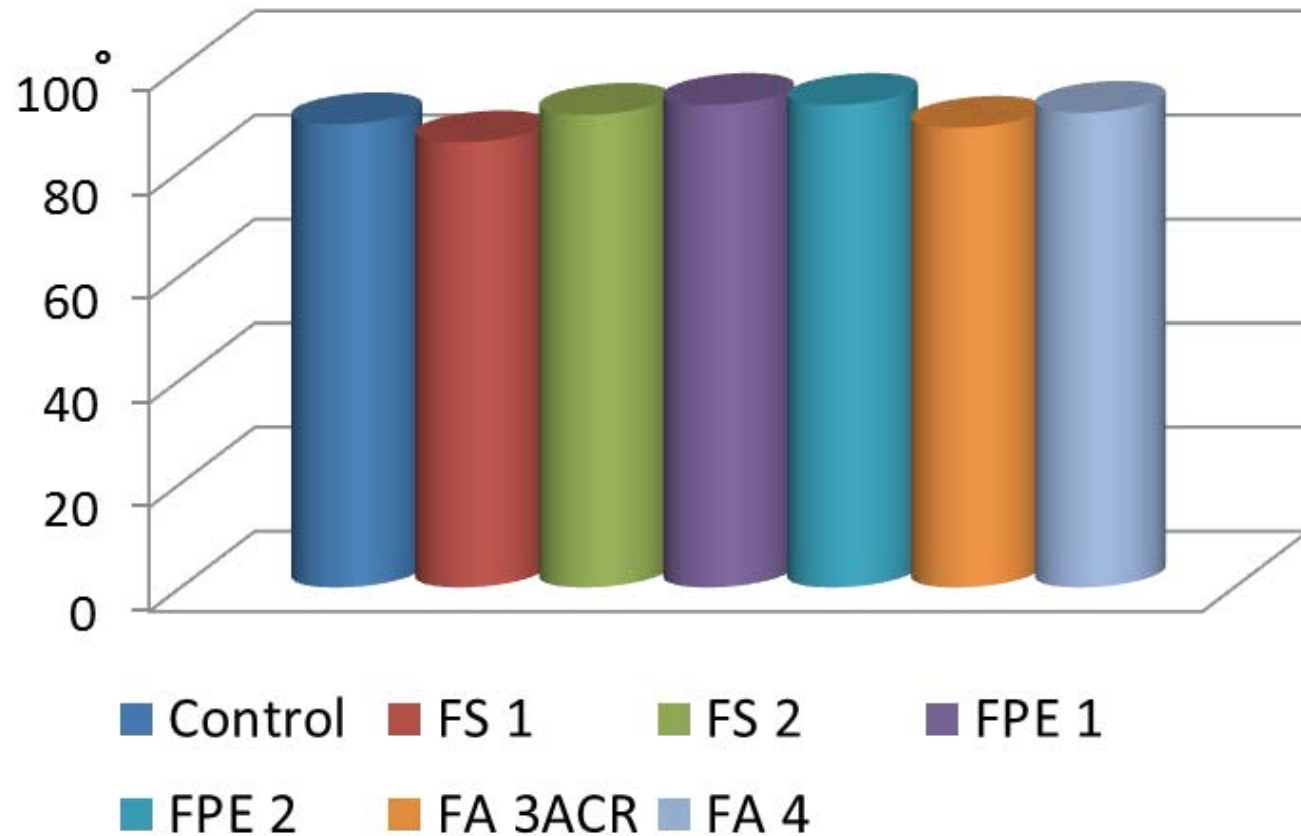


# Gloss: UV Urethane Acrylate



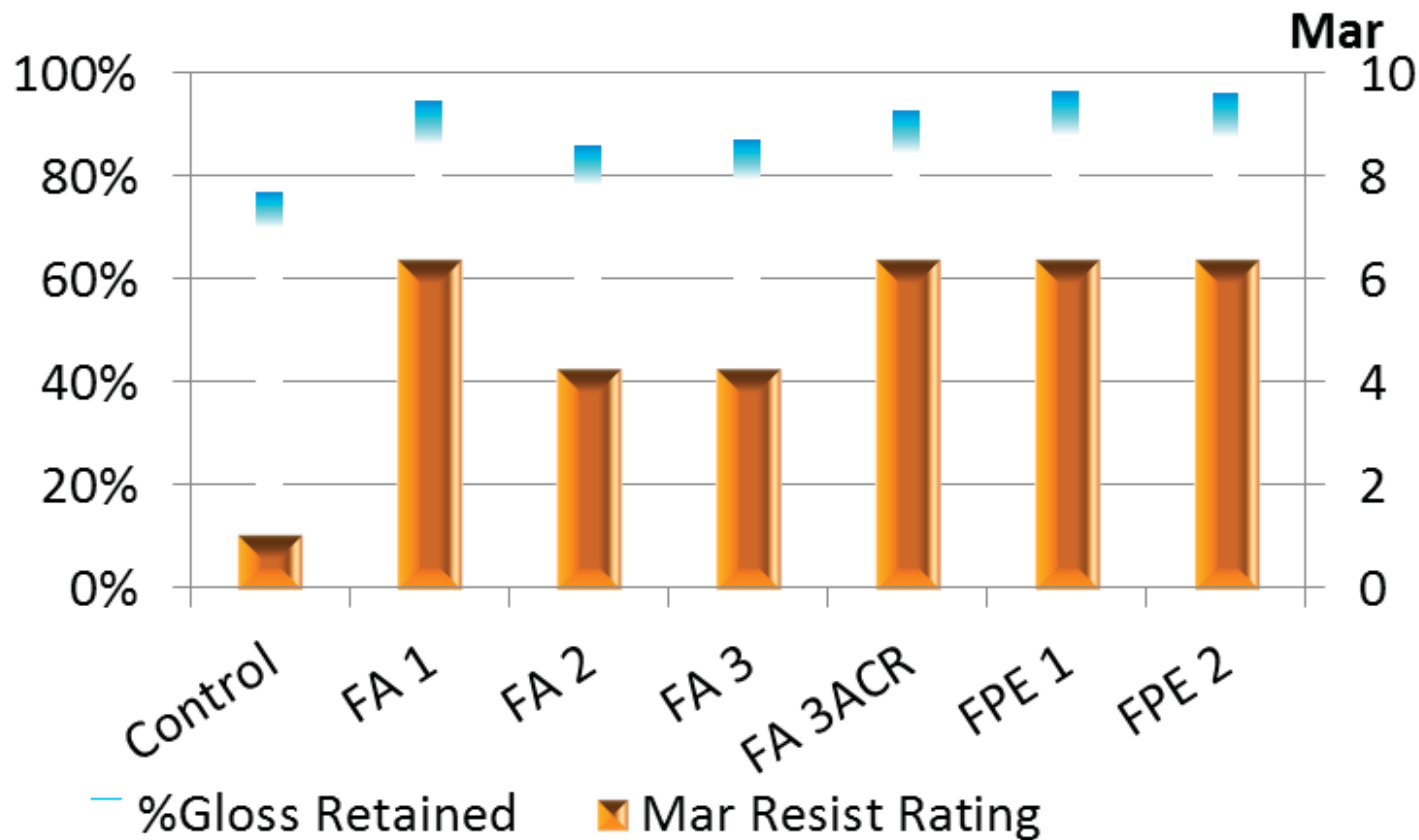
- FPE are most miscible, keep gloss
- FA and FS types decrease gloss

# Gloss: UV Epoxy Acrylate



- Minor incompatibility

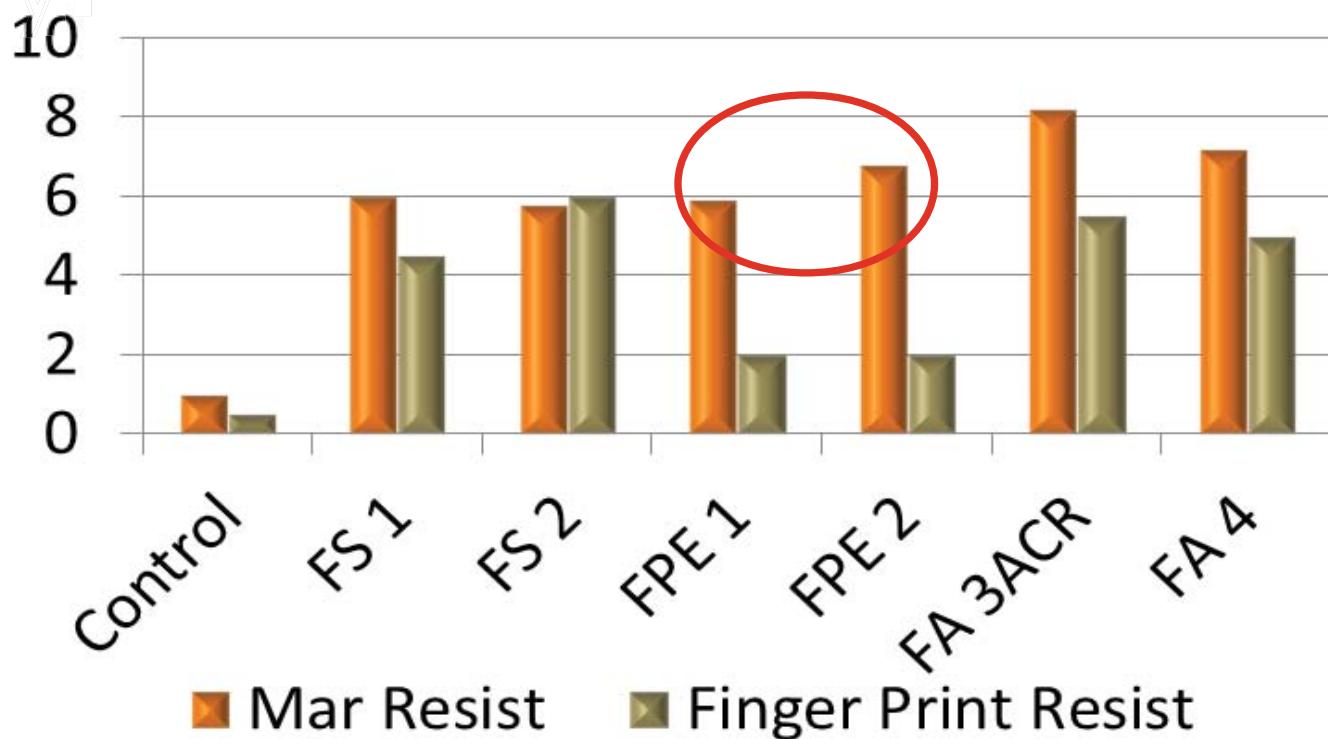
# Mar Resist: SB Urethane



- All improve mar resistance

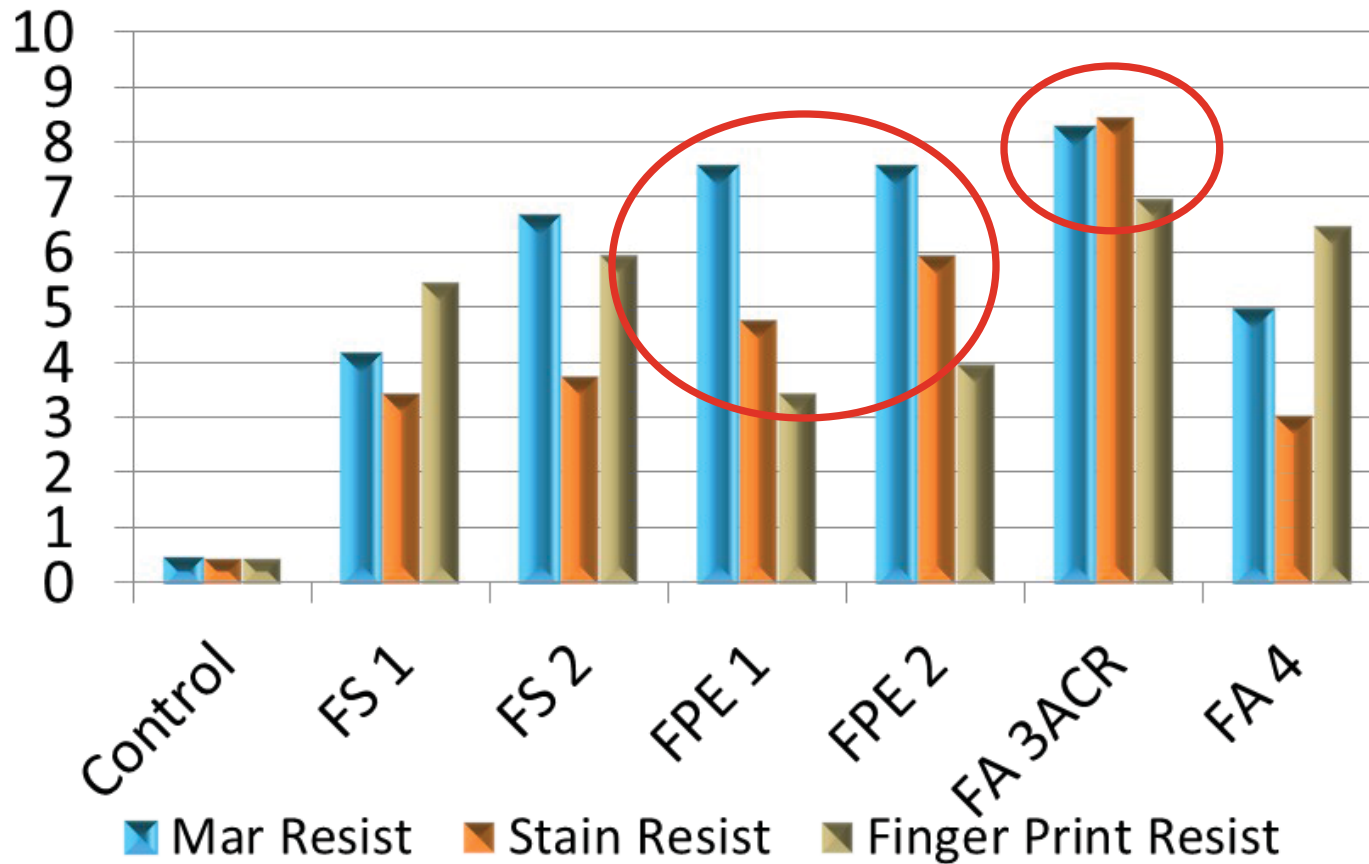


# Mar/ Finger Print: UV Ureth. Acry



- All improve mar resistance
- All improve anti-finger print

# Mar, Stain, Print: UV Epoxy Acrylate



- All improved, more with %sil
- FPEs weak on fingerprint
- FA3 ACP strong on all

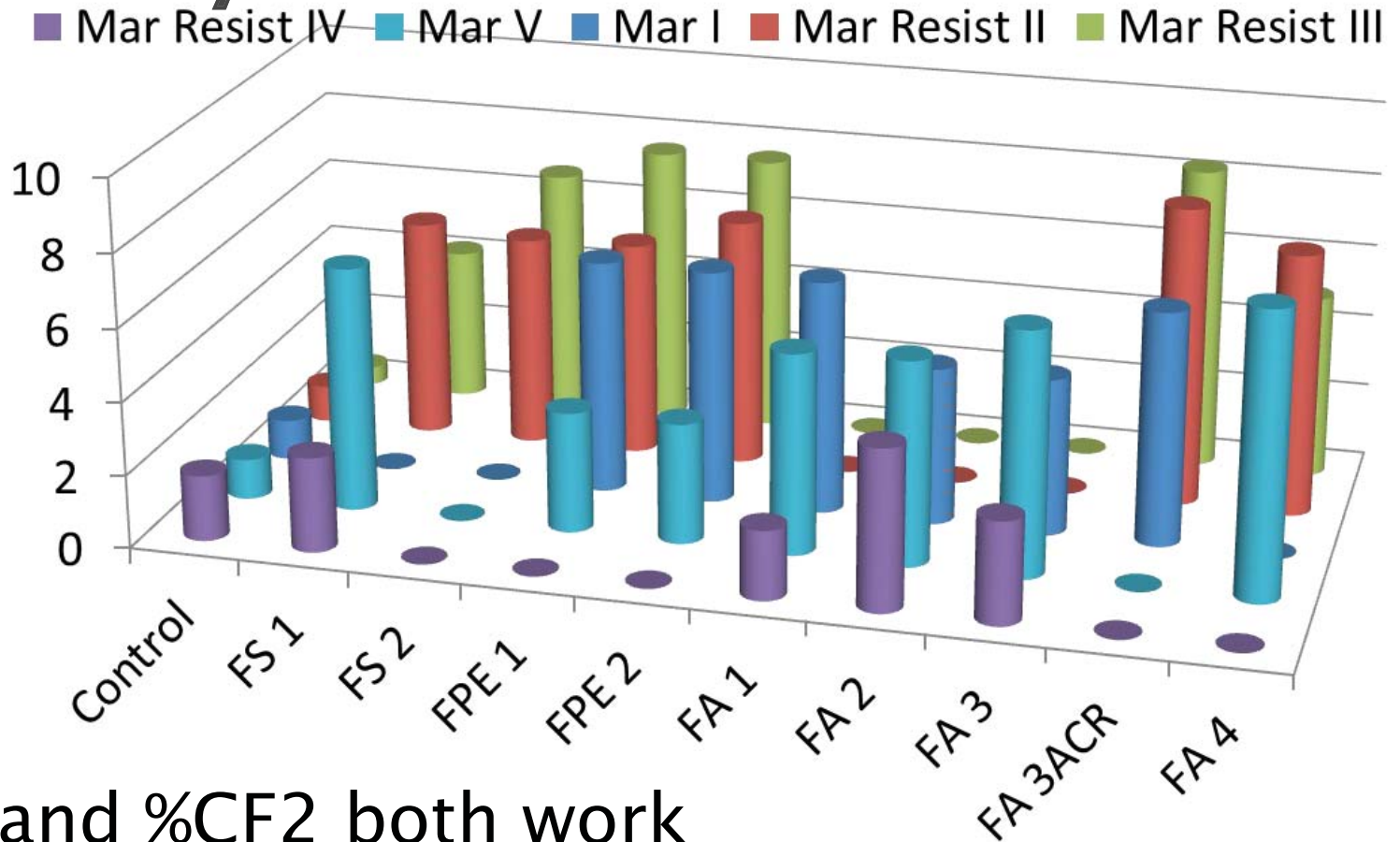


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# Summary

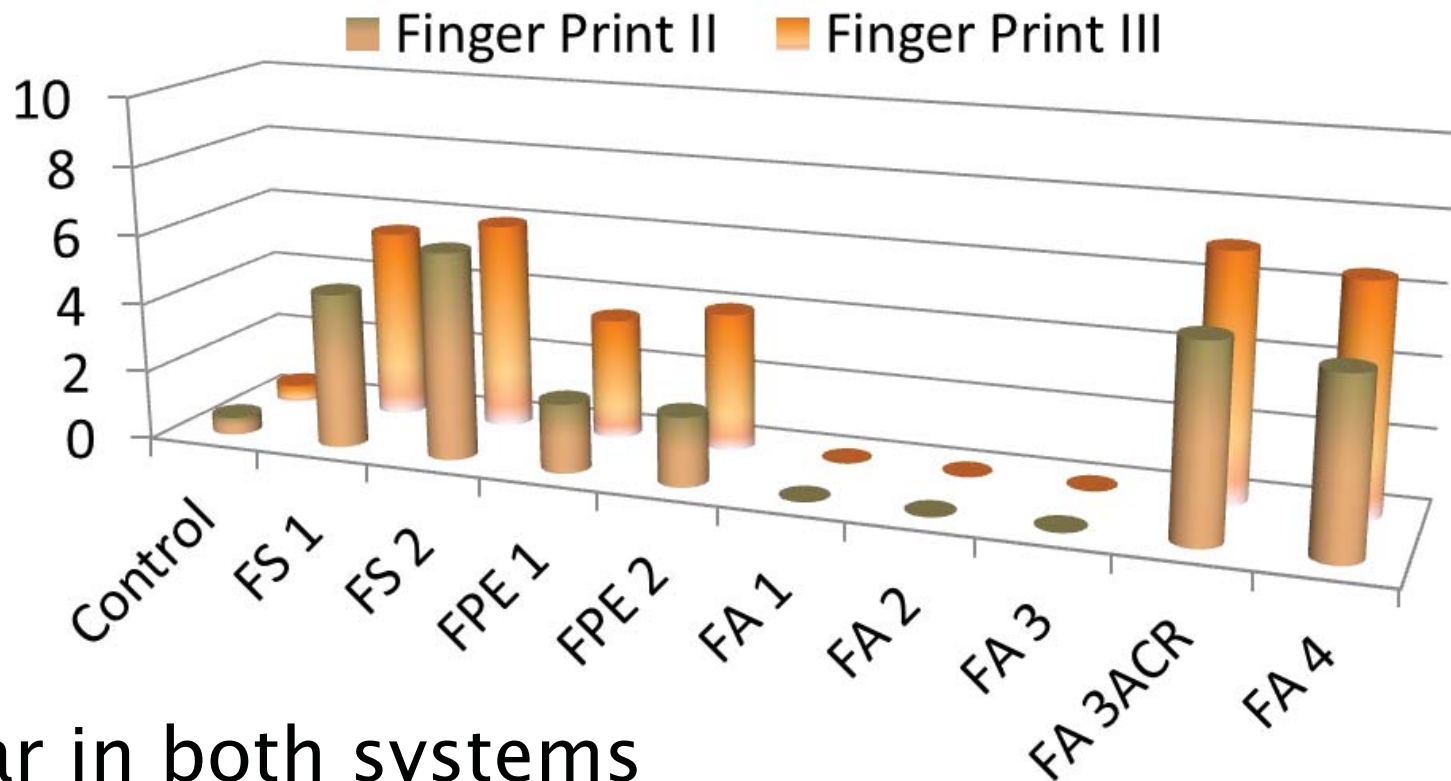
## Mar



- %SiI and %CF<sub>2</sub> both work
- FA 3 ACR is very good
- FPEs are very good

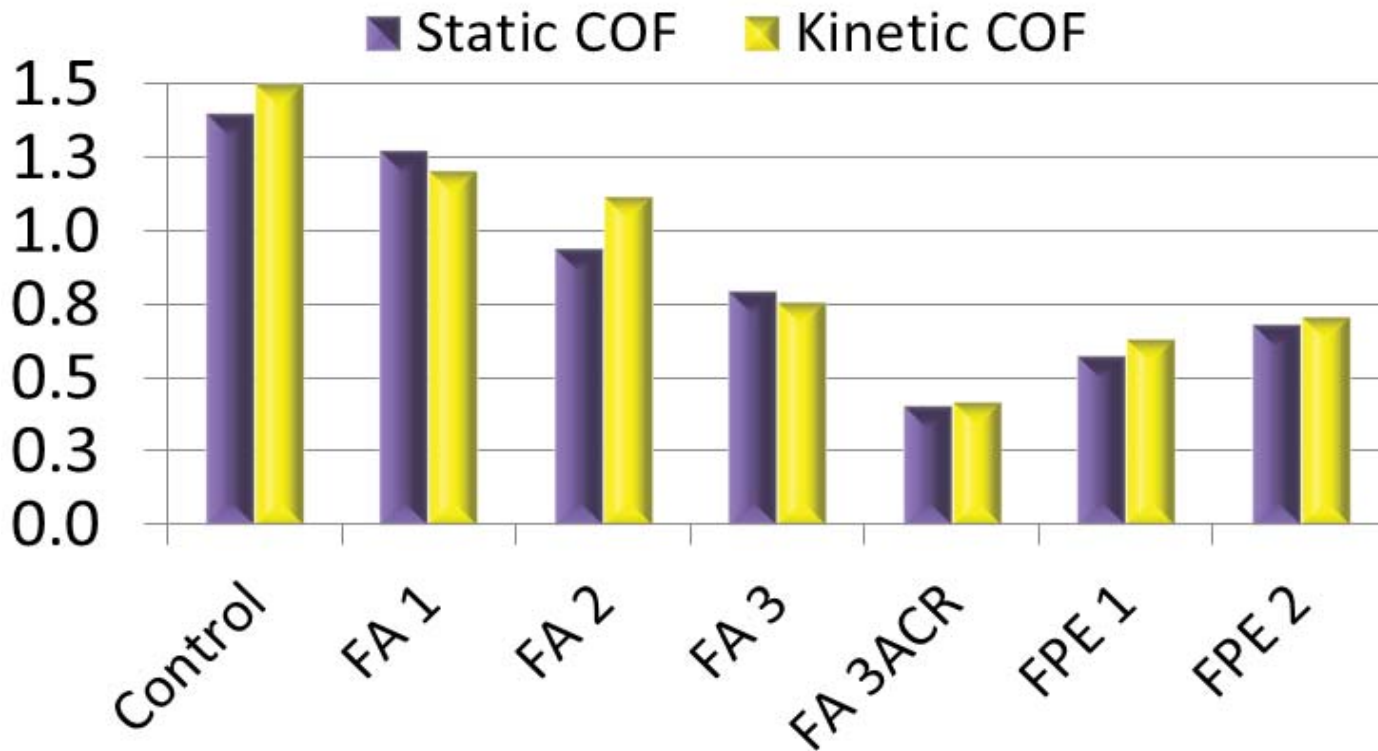


# Summary Fingerprint



- Similar in both systems
- High CF2 content works
- But best has both

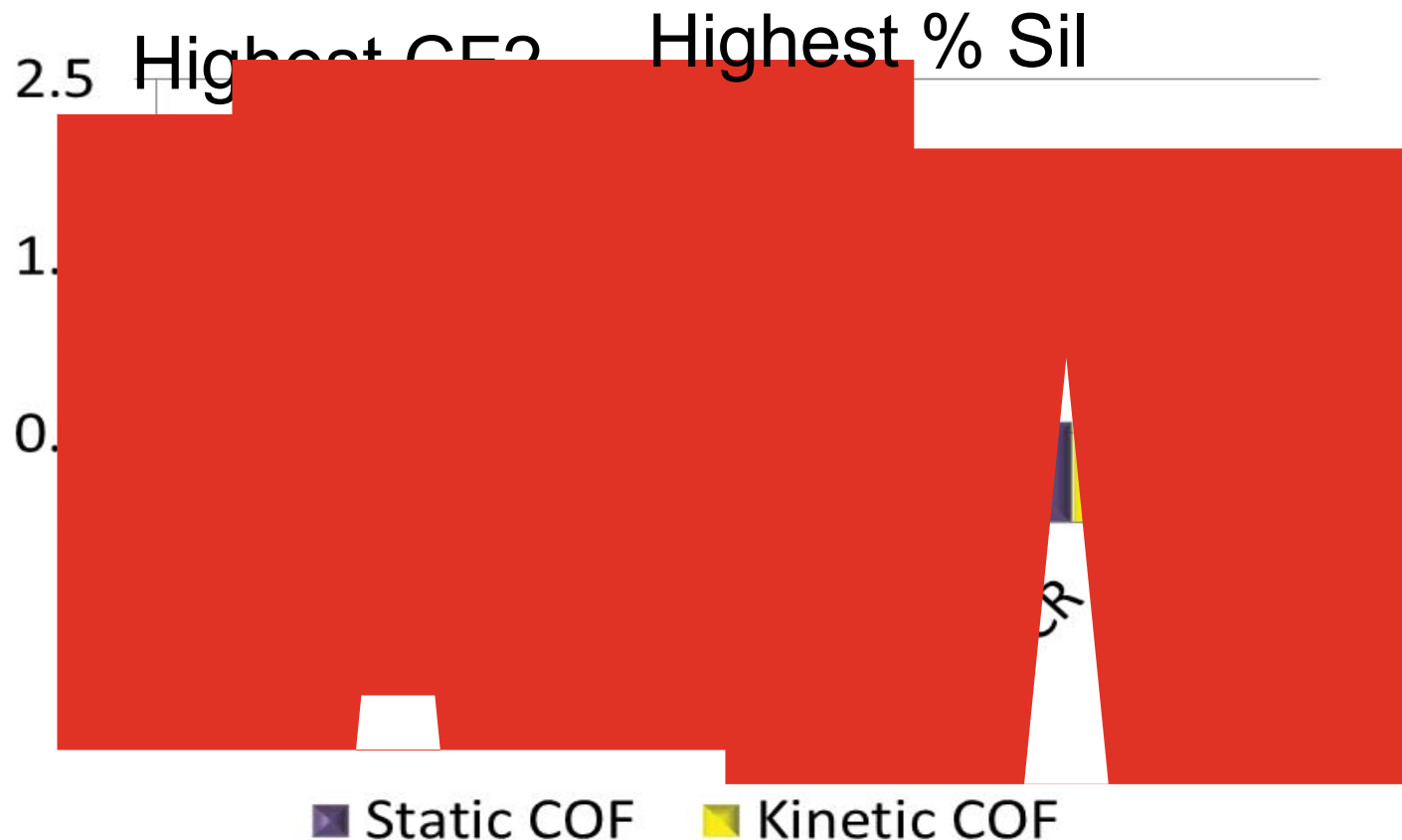
# COF Reduction: SB Urethane



- All improve COF
- More with  $>$  wt% silicone

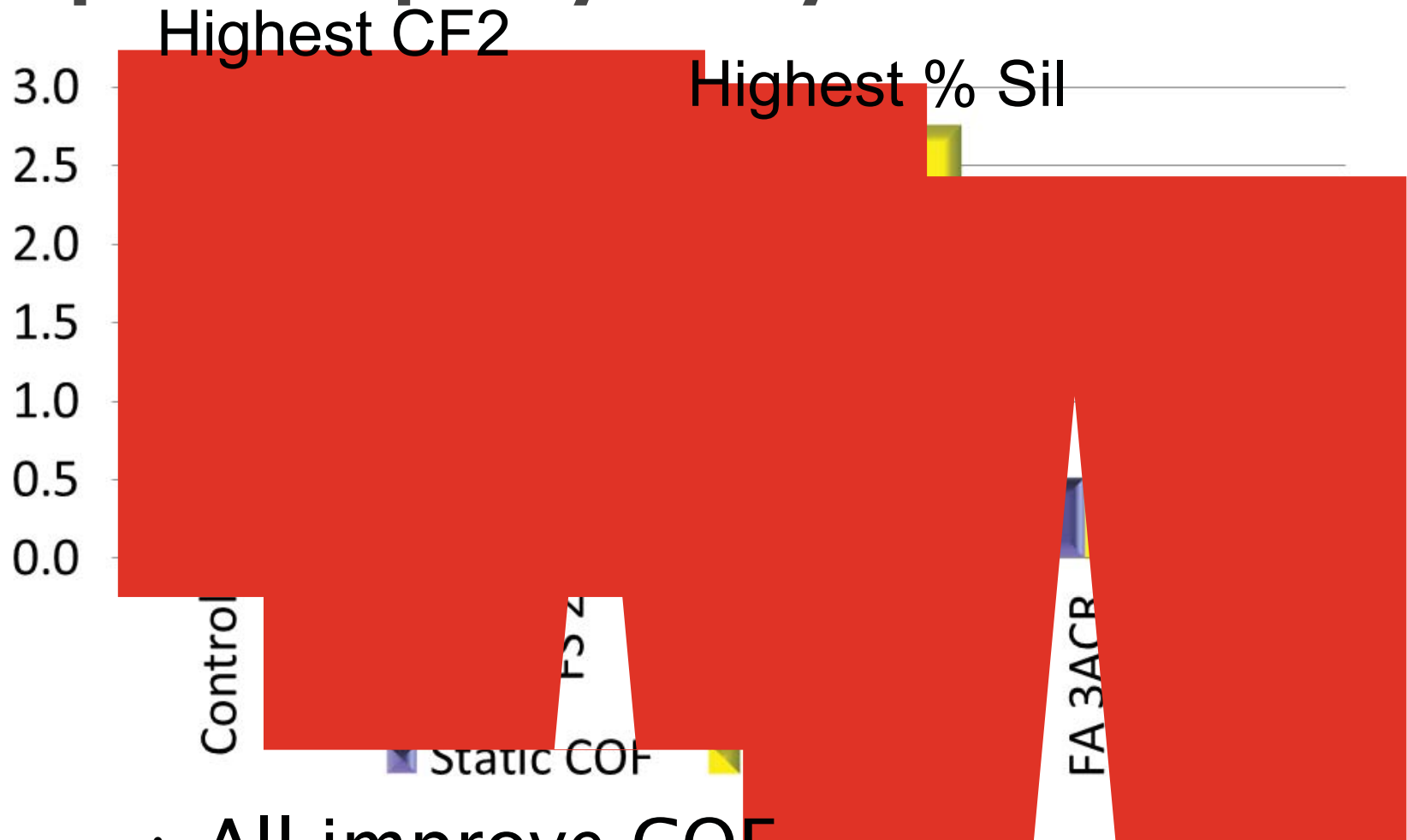


# Slip: UV Urethane Acrylate



- All improve COF
- More with > wt% CF<sub>2</sub>

# Slip: UV Epoxy Acrylate



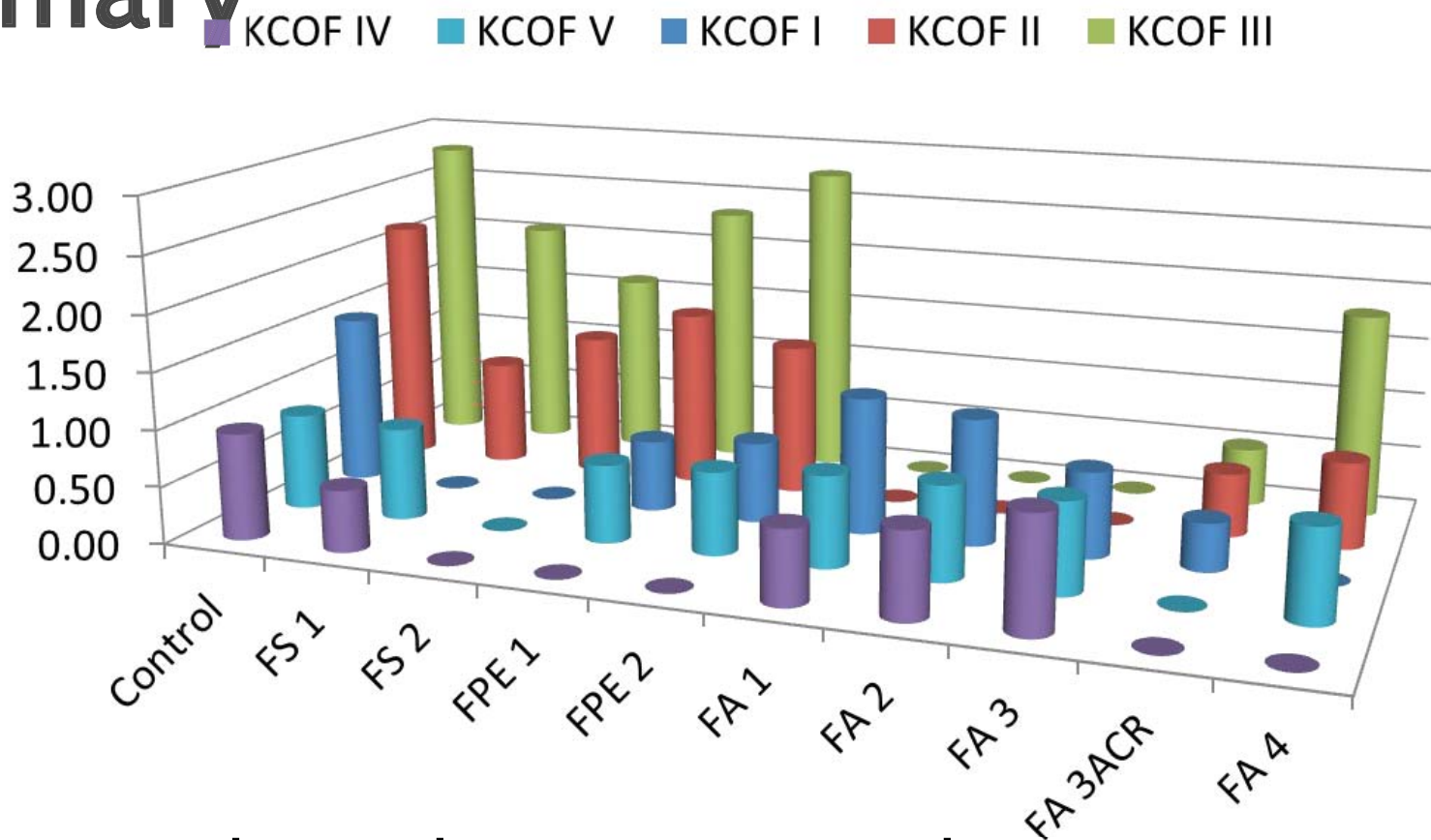
- All improve COF
- More with > wt% silicone



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# Summary Slip



- FA 3ACR with moderate %CF2 is best
- FPEs, FS1 are good

# Stain Resistant: SB Urethane

|         | HB Pencil | Black permanent marker | Blue pencil Crayon | Brown Crayon | Black Crayon | Average Stain |
|---------|-----------|------------------------|--------------------|--------------|--------------|---------------|
| Control | 1.7       | 1.7                    | 1.7                | 1.0          | 1.0          | 1.4           |
| FA 1    | 5.0       | 4.2                    | 8.3                | 8.0          | 8.0          | 6.7           |
| FA 2    | 5.0       | 5.0                    | 4.2                | 10.0         | 9.0          | 6.6           |
| FA 3    | 7.5       | 7.5                    | 6.7                | 10.0         | 3.0          | 6.9           |
| FA 3ACR | 6.7       | 7.5                    | 8.3                | 7.0          | 8.0          | 7.5           |
| FPE 1   | 6.7       | 7.5                    | 5.0                | 4.0          | 7.0          | 6.0           |
| FPE 2   | 6.7       | 5.0                    | 8.3                | 5.0          | 6.0          | 6.2           |

# Stain Resist: UV Urethane Acrylate

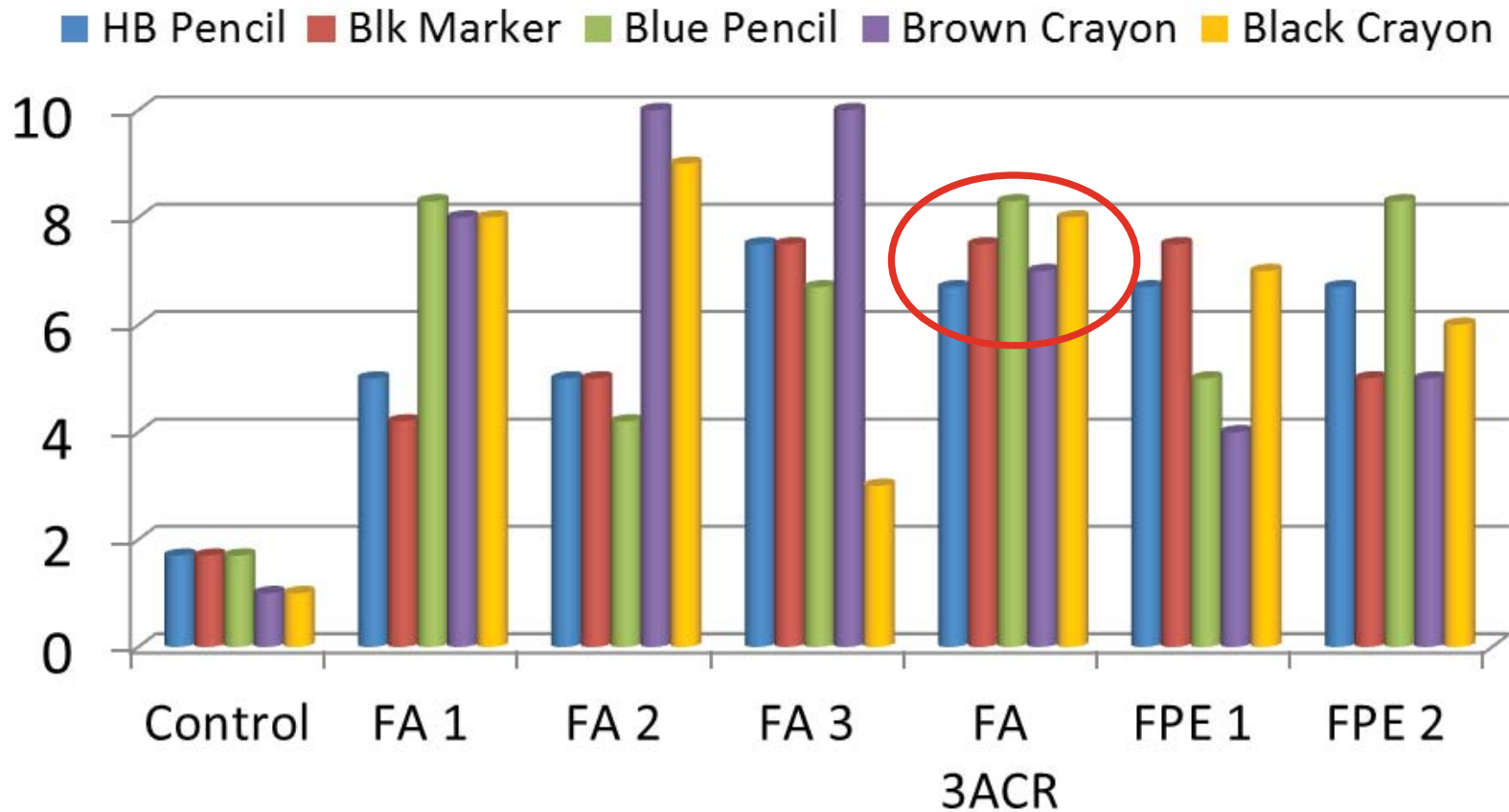
|         | HB Pencil | Black Crayons | Brown Crayon | Red pencil crayon | Blue pencil crayon | Black permanent marker | Average |
|---------|-----------|---------------|--------------|-------------------|--------------------|------------------------|---------|
| Control | 2.0       | 1.7           | 1.7          | 1.6               | 1.6                | 1.5                    | 1.7     |
| FS 1    | 4.2       | 3.3           | 3.3          | 5.0               | 5.0                | 3.3                    | 4.0     |
| FS 2    | 6.7       | 8.3           | 8.3          | 5.0               | 6.7                | 5.0                    | 6.7     |
| FPE 1   | 6.7       | 10.0          | 10.0         | 6.7               | 6.7                | 5.8                    | 7.6     |
| FPE 2   | 6.7       | 10.0          | 10.0         | 6.7               | 6.7                | 5.8                    | 7.6     |
| FA 3ACR | 8.0       | 10.0          | 10.0         | 8.0               | 8.0                | 6.0                    | 8.3     |
| FA 4    | 5.0       | 5.0           | 5.0          | 5.0               | 5.0                | 5.0                    | 5.0     |

# Stain: UV Epoxy Acrylate

|         | HB Pencil | Black Crayon | Brown Crayon | Red pencil crayon | Blue pencil crayon | Black permanent marker | Average |
|---------|-----------|--------------|--------------|-------------------|--------------------|------------------------|---------|
| Control | 0.6       | 0.4          | 0.4          | 0.5               | 0.5                | 0.3                    | 0.5     |
| FS 1    | 5.0       | 5.0          | 5.0          | 4.0               | 4.0                | 2.3                    | 4.2     |
| FA 4    | 6.0       | 5.5          | 5.5          | 5.0               | 5.0                | 3.0                    | 5.0     |
| FS 2    | 7.0       | 8.0          | 8.0          | 6.0               | 6.0                | 5.4                    | 6.7     |
| FPE 2   | 7.5       | 9.0          | 9.0          | 8.0               | 8.0                | 4.0                    | 7.6     |
| FPE 1   | 7.5       | 9.0          | 9.0          | 8.0               | 8.0                | 4.0                    | 7.6     |
| FA 3ACR | 10.0      | 9.0          | 6.0          | 8.0               | 8.0                | 9.0                    | 8.3     |



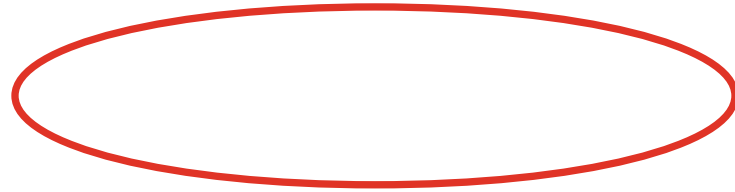
# Stain Resist: SB Urethane



- In this view, FA 3 and FA 3 ACR are strong

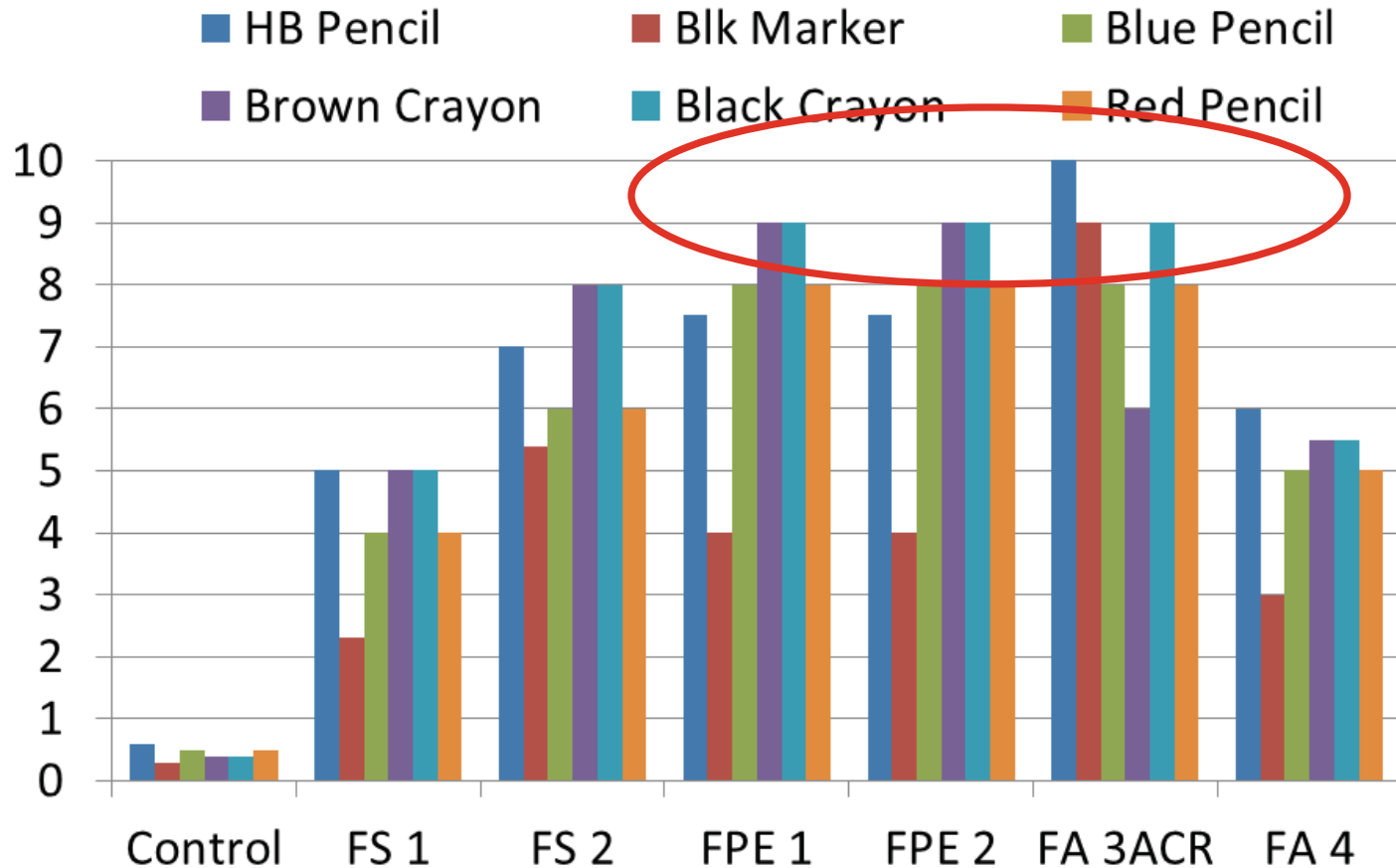


# Stain Resist: UV Urethane Acrylate



- FA 3 ACR and FPEs are effective

# Stain: UV Epoxy Acrylate



- Highest %CF2 is least effective
- FA 3 ACR and FPEs are effective

# Summary:

- ▶ All FAS additives improve COF, mar and stain resistance and to a lesser degree fingerprint resist.
- ▶ FPE are the only compatible FASs and give good slip, mar and anti stain, but weak finger print resist
- ▶ FA 3ACR, FPE 1 & FPE 2 again give relatively high ratings for gloss, mar and stain resistance.
- ▶ Best results for crayons
- ▶ FS 2, FA 4 & FA 3ACR give the best fingerprint resist.
- ▶ FA 4 – which has a balance of % SiI, %CF<sub>2</sub>, & %CH<sub>2</sub> – again gives a very good balance of properties.



# System: Cationic Silicone Resin

An in house, all silicone epoxy resin based cationic UV epoxy cured system uses a cycloaliphatic epoxy silicone (Silmer EPC E9 from Siltech) with the relevant percentage of FAS (0.2%, 0.5%, 1%, 3%, 5%) added, along with 0.5% UV9380C by Momentive (a cationic catalyst for UV curing.) Formulations were as follows:

|      | A   | B   | C  | D  | E  | F   | G   | H  | I  | J  | K   | L   | M  | N  | O  | P | Q | R | S | T |
|------|-----|-----|----|----|----|-----|-----|----|----|----|-----|-----|----|----|----|---|---|---|---|---|
| FS 1 | .2% | .5% | 1% | 3% | 5% |     |     |    |    |    |     |     |    |    |    |   |   |   |   |   |
| FA 3 |     |     |    |    |    | .2% | .5% | 1% | 3% | 5% |     |     |    |    |    |   |   |   |   |   |
| FA 1 |     |     |    |    |    |     |     |    |    |    | .2% | .5% | 1% | 3% | 5% |   |   |   |   |   |
| FA 2 |     |     |    |    |    |     |     |    |    |    |     |     |    |    |    |   |   |   |   |   |

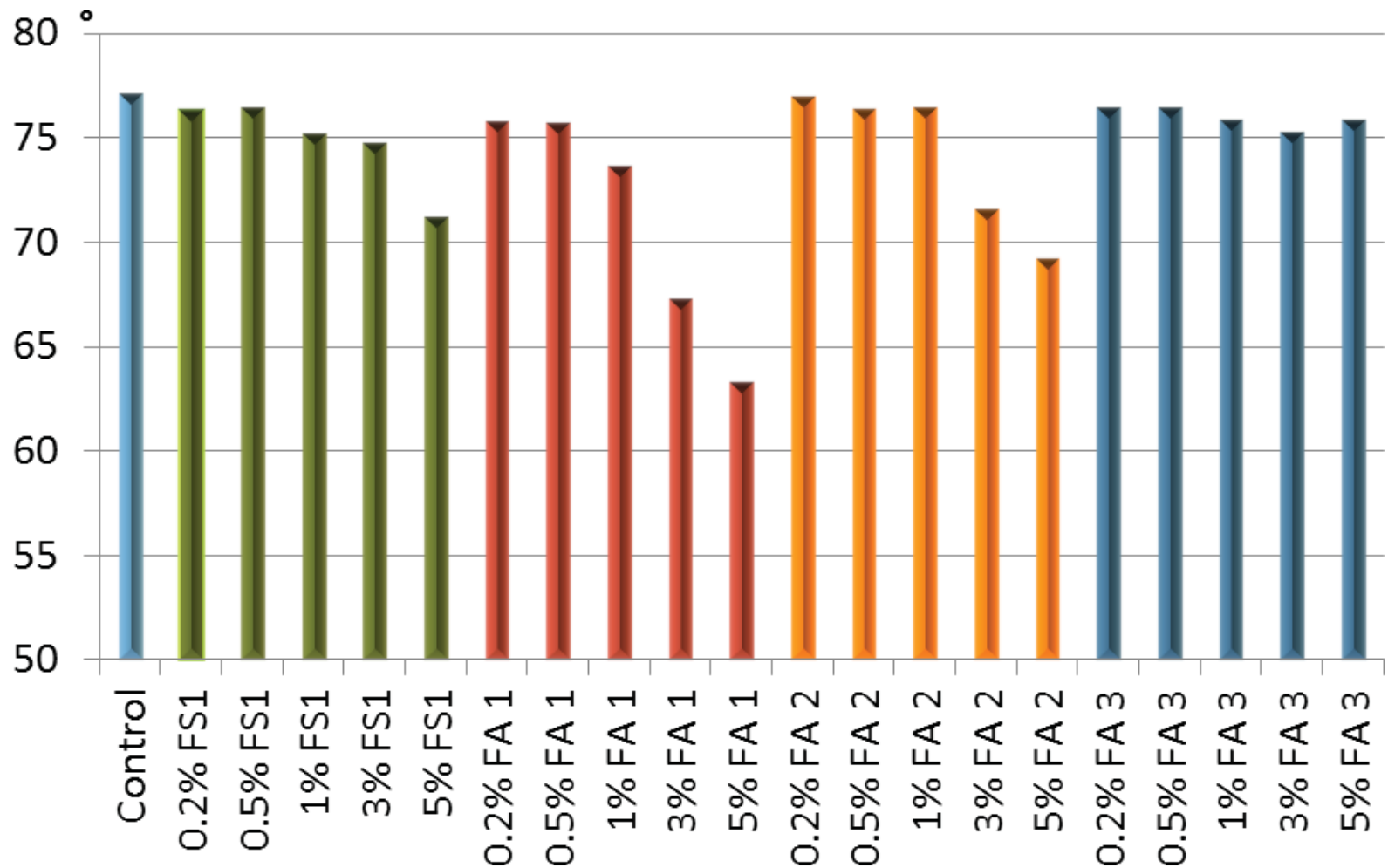
- Drawn down on Leneta paper with a wire wound rod #10.
- Cured with a 10 mW/cm<sup>2</sup> UV box for 1 hour
- Kept at room temperature for one day



# Film Properties: Cationic

| Additive | %FAS | Static COF | Kinetic COF | Gloss | %Gloss Retained | Mar Resistance | Stain Resistance | Appearance |
|----------|------|------------|-------------|-------|-----------------|----------------|------------------|------------|
| Control  | 0%   | 1.188      | 0.94        | 77.1  | 17.8%           | 1.8            | 2.4              | Smooth     |
| FS1      | 0.2% | 0.782      | 0.758       | 76.3  | 28.4%           | 2.8            | 2.4              | Smooth     |
| FS1      | 0.5% | 0.639      | 0.648       | 76.5  | 26.2%           | 2.6            | 2.8              | Smooth     |
| FS1      | 1.0% | 0.549      | 0.545       | 75.2  | 26.2%           | 2.6            | 3.6              | Smooth     |
| FS1      | 3.0% | 0.528      | 0.508       | 74.8  | 39.0%           | 3.9            | 4.7              | Smooth     |
| FS1      | 5.0% | 0.582      | 0.583       | 71.2  | 27.1%           | 2.7            | 6.1              | Smooth     |
| FA 3     | 0.2% | 0.977      | 0.789       | 76.5  | 18.0%           | 1.8            | 2.7              | Smooth     |
| FA 3     | 0.5% | 1.221      | 1.084       | 76.5  | 18.0%           | 1.8            | 2.8              | Smooth     |
| FA 3     | 1.0% | 1.182      | 1.001       | 75.9  | 28.3%           | 2.8            | 4.3              | Smooth     |
| FA 3     | 3.0% | 0.955      | 0.905       | 75.3  | 28.7%           | 2.9            | 5.3              | Smooth     |
| FA 3     | 5.0% | 1.256      | 1.236       | 75.9  | 18.9%           | 1.9            | 5.9              | Smooth     |
| FA 1     | 0.2% | 1.147      | 1.005       | 75.8  | 54.5%           | 5.4            | 2.9              | Smooth     |
| FA 1     | 0.5% | 1.149      | 0.883       | 75.7  | 64.8%           | 6.5            | 3.3              | Smooth     |
| FA 1     | 1.0% | 0.764      | 0.656       | 73.7  | 18.9%           | 1.9            | 4.1              | Smooth     |
| FA 1     | 3.0% | 1.257      | 1.128       | 67.3  | 32.9%           | 3.3            | 4.8              | Smooth     |
| FA 1     | 5.0% | 1.265      | 1.262       | 63.3  | 28.9%           | 2.9            | 6.0              | Smooth     |
| FA 2     | 0.2% | 1.262      | 1.12        | 77.0  | 43.5%           | 4.4            | 3.1              | Smooth     |
| FA 2     | 0.5% | 1.158      | 1.129       | 76.4  | 35.1%           | 3.5            | 3.6              | Smooth     |
| FA 2     | 1.0% | 0.791      | 0.754       | 76.5  | 43.9%           | 4.4            | 4.4              | Smooth     |
| FA 2     | 3.0% | 1.179      | 1.114       | 71.6  | 33.3%           | 3.3            | 5.3              | Smooth     |
| FA 2     | 5.0% | 1.215      | 1.093       | 69.2  | 25.7%           | 2.6            | 5.8              | Smooth     |

# Gloss: Cationic UV Silicone



• Impact of use level

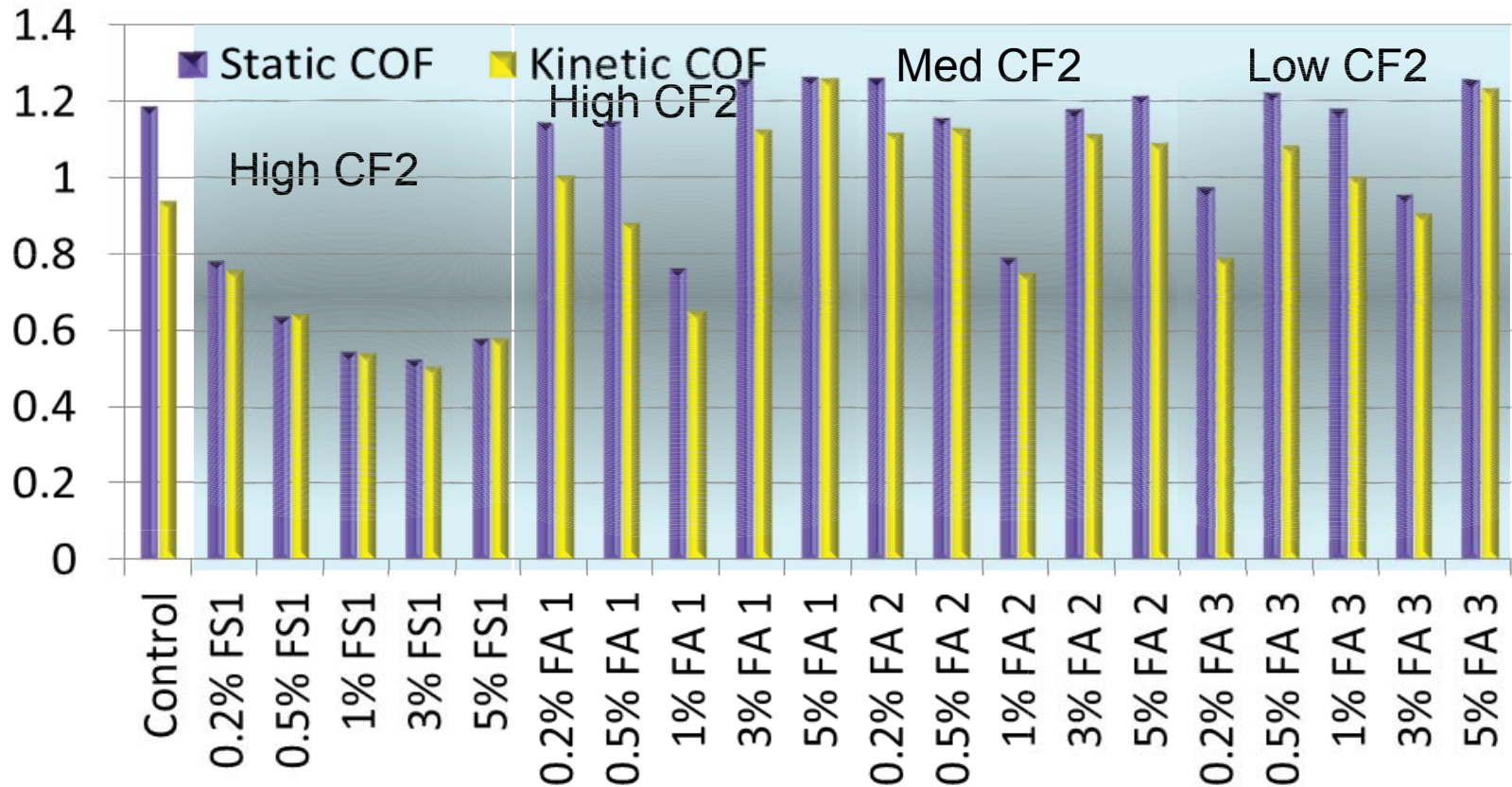


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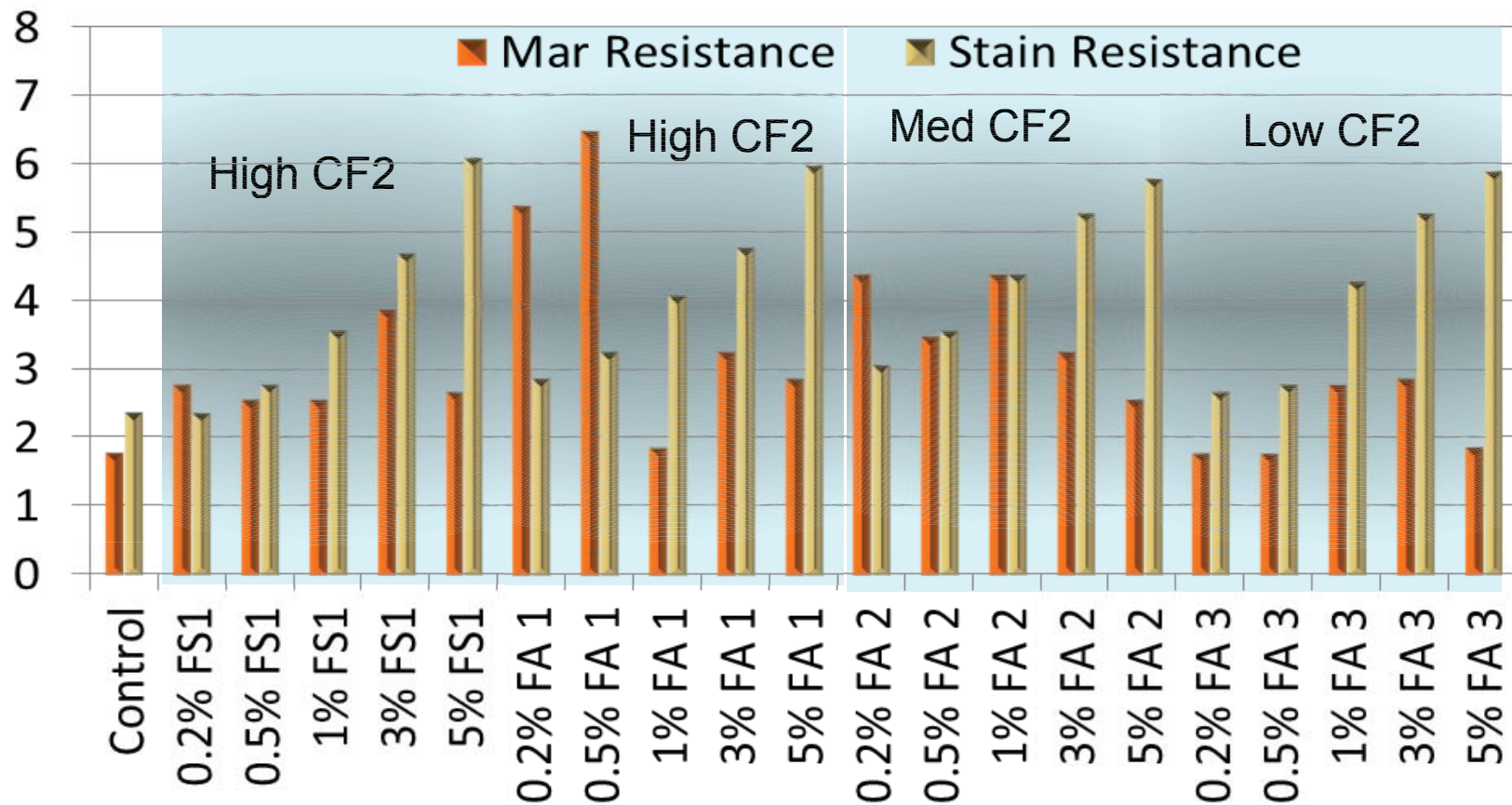
# Slip: Cationic Epoxy Silicone



- High CF2 content lowers COF
- High use levels lowers COF



# Stain and Mar: Cationic



- Use level has most impact on stain
- Low CF2 FAS just as good as high CF2

# Summary: Cationic Epoxy Silicone

- All FAS are compatible with silicone epoxy resin.
- 60° Gloss is slightly reduced and no surface defects are seen. More FAS does lower gloss more.
- Most FAS show improvements to mar resistance. This is seen at low use levels and barely improved or somewhat lost at higher use levels.
- Only FS 1 – with the highest CF<sub>2</sub> content – shows the dramatic lowering of COF that one usually sees with silicone or fluoroalkyl additives.
- Stain resistance was similar for each additive, stain dependent, and increased with use level of FAS.



# Stain summary

- ▶ High % Silicone FAS materials are best on Graphite, WB and Waxy stains
- ▶ High % CF<sub>2</sub> better for waxes but still not as good as above
- ▶ High MW makes little difference
- ▶ More is better

# Summary of film properties

|         | Compatible                 |                            |                     |                              |           | Slip                       |                            |                     |                              |           | Mar                        |                            |                     |                              |           |
|---------|----------------------------|----------------------------|---------------------|------------------------------|-----------|----------------------------|----------------------------|---------------------|------------------------------|-----------|----------------------------|----------------------------|---------------------|------------------------------|-----------|
|         | SB<br>Ur<br>eth<br>an<br>e | UV<br>Ur<br>eth<br>an<br>e | UV<br>Ep<br>ox<br>y | Cat<br>.<br>Sili<br>co<br>ne | Pai<br>nt | SB<br>Ur<br>eth<br>an<br>e | UV<br>Ur<br>eth<br>an<br>e | UV<br>Ep<br>ox<br>y | Cat<br>.<br>Sili<br>co<br>ne | Pai<br>nt | SB<br>Ur<br>eth<br>an<br>e | UV<br>Ur<br>eth<br>an<br>e | UV<br>Ep<br>ox<br>y | Cat<br>.<br>Sili<br>co<br>ne | Pai<br>nt |
| FPE 1   | ++                         | ++                         | ++                  |                              | ++        | ++                         | +                          | +                   |                              | -         | ++                         | ++                         | ++                  |                              | +         |
| FPE 2   | ++                         | ++                         | ++                  |                              | ++        | ++                         | +                          | +                   |                              | -         | ++                         | ++                         | ++                  |                              | +         |
| FS 1    |                            | -                          | -                   | +                            | -         |                            | ++                         | +                   | ++                           | -         |                            | ++                         | +                   | +                            | +         |
| FS 2    |                            | -                          | +                   |                              |           |                            | +                          | +                   |                              |           |                            | ++                         | +                   |                              |           |
| FA 1    | -                          |                            |                     | -                            | -         | -                          |                            |                     | -                            | -         | ++                         |                            |                     | -                            | ++        |
| FA 2    | +                          |                            |                     | -                            | -         | +                          |                            |                     | -                            | -         | +                          |                            |                     | -                            | ++        |
| FA 3    | +                          |                            |                     | +                            | -         | +                          |                            |                     | -                            | -         | +                          |                            |                     | -                            | ++        |
| FA 3ACR | -                          | -                          | +                   |                              |           | ++                         | ++                         | ++                  |                              |           | ++                         | ++                         | ++                  |                              |           |
| FA 4    |                            | -                          | +                   |                              | -         |                            | ++                         | +                   |                              | -         |                            | ++                         | +                   |                              | ++        |



# Summary of film properties

|         | Average Stain  |                |             |                  |       | Finger print   |             |
|---------|----------------|----------------|-------------|------------------|-------|----------------|-------------|
|         | SB<br>Urethane | UV<br>Urethane | UV<br>Epoxy | Cat.<br>Silicone | Paint | UV<br>Urethane | UV<br>Epoxy |
| FPE 1   | +              | +              | ++          |                  | -     | +              | +           |
| FPE 2   | +              | +              | ++          |                  | -     | +              | +           |
| FS 1    |                | +              | +           | +                | -     | +              | ++          |
| FS 2    |                | ++             | +           |                  |       | ++             | ++          |
| FA 1    | ++             |                |             | ++               | -     |                |             |
| FA 2    | ++             |                |             | ++               | -     |                |             |
| FA 3    | ++             |                |             | ++               | -     |                |             |
| FA 3ACR | ++             | ++             | ++          |                  |       | ++             | ++          |
| FA 4    |                | ++             | +           |                  | -     | ++             | ++          |

# WB Stain Resistance Summary

|         | Ink                  | Black marker       |                    |                 |                      |       | Juices |                      |
|---------|----------------------|--------------------|--------------------|-----------------|----------------------|-------|--------|----------------------|
|         | Cat.<br>Silic<br>one | SB<br>Uret<br>hane | UV<br>Uret<br>hane | UV<br>Epox<br>y | Cat.<br>Silic<br>one | Paint | Paint  | Cat.<br>Silic<br>one |
| FPE 1   |                      | ++                 | ++                 | +               |                      | -     | -      |                      |
| FPE 2   |                      | +                  | ++                 | +               |                      | -     | ++     |                      |
| FS 1    | ++                   |                    | -                  | -               | ++                   | +     | -      | +                    |
| FS 2    |                      |                    | +                  | +               |                      |       |        |                      |
| FA 1    | +                    | +                  |                    |                 | +                    | +     | +      | +                    |
| FA 2    | +                    | +                  |                    |                 | +                    | ++    | ++     | ++                   |
| FA 3    | +                    | ++                 |                    |                 | +                    | ++    | ++     | ++                   |
| FA 3ACR |                      | ++                 | ++                 | ++              |                      |       |        |                      |
| FA 4    |                      |                    | +                  | +               |                      | +     | ++     |                      |



# Waxy Stain Resistance

## Summary

|         | Crayon             |                    |                 | Pencil Crayon |                 |                      | Silicone Pigment     |       |
|---------|--------------------|--------------------|-----------------|---------------|-----------------|----------------------|----------------------|-------|
|         | SB<br>Uret<br>hane | UV<br>Uret<br>hane | UV<br>Epox<br>y | Uret<br>hane  | UV<br>Epox<br>y | Cat.<br>Silic<br>one | Cat.<br>Silic<br>one | Paint |
| FPE 1   | +                  | ++                 | ++              | ++            | ++              |                      |                      | ++    |
| FPE 2   | +                  | ++                 | ++              | ++            | ++              |                      |                      | ++    |
| FS 1    |                    | -                  | ++              | +             | +               | ++                   | -                    | -     |
| FS 2    |                    | ++                 | ++              | +             | +               |                      |                      |       |
| FA 1    | ++                 |                    |                 |               |                 | ++                   | +                    | -     |
| FA 2    | ++                 |                    |                 |               |                 | ++                   | +                    | +     |
| FA 3    | +                  |                    |                 |               |                 | ++                   |                      | +     |
| FA 3ACR | ++                 | ++                 | ++              | +             | ++              |                      |                      |       |
| FA 4    |                    | +                  | +               | +             | +               |                      |                      | -     |





# Recommendations

- ▶ FSE 1, FSE 2 are available as Fluorosil® 2010, Fluorosil 2110. These are very good for all but fingerprint resistance
- ▶ R&D product FA3 and FA3 ACR is best overall including for fingerprint resistance. It is not always compatible.
- ▶ Use levels are up to 5% and more is better in most cases.



# Thank you