Advancement in PTFE Dispersions for Electroless Nickel Codeposition

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A new generation of PTFE dispersion provides a significantly higher PTFE content and broader range of PTFE (0.5 to 13 wt%) incorporation into electroless nickel coatings. The dispersion and subsequent codeposition properties of the new system are compared to two older PTFE dispersions containing PFOS and a current system that is PFOS-free. Deposit properties such as coefficient of friction, surface roughness, surface profile, PTFE content, hardness and wear are presented.

Keywords: *Electroless nickel, codeposition, PTFE.*

Introduction

Many commercially available polytetrafluoroethylene (PTFE) dispersions have been introduced since the early 1990s for the codeposition of PTFE with electroless nickel. The technology has come a long way in the last 20 years. The systems are basically still the same, a mixture of PTFE particles, surfactants and water. The PTFE particles are suspended as an emulsion in the electroless nickel plating bath. The PTFE particles are attracted to the plating surface by a charge provided by the wetting agents, and become uniformly incorporated in the deposit. The deposited coating is comprised of nickel, 8 to 9 wt% phosphorus and PTFE particles. The amount of PTFE codeposited depends on many factors: temperature, pH, particle size, solution age, agitation, concentration of PTFE particles, and the amount and type of surfactants used.

Subsequently, the processes that are now available have the advantage of being the successors to countless dispersions that have been developed and marketed. The newer systems boast a longer bath life. No longer limited to one metal turn-over (MTO) before the PTFE falls out of solution, many baths can now be maintained for two to three MTOs. The PTFE content in deposit has increased with time and dispersions can now provide a larger operating window than previous systems.

The phase-out of perfluorooctanesulfonic acid (PFOS) and perfluorooctanoic acid (PFOA) surfactants provided a challenge. It became essential to find more environmentally friendly chemicals to use in the PTFE dispersions. Consequently, several PFOS-free systems became commercially available earlier this decade. Building on 20 years of research and development, a second generation of PFOS-free dispersions is now being presented, that continue to surpass previous versions.

In this paper, four PTFE dispersions are compared based on physical and mechanical properties. Two of the systems are dispersions containing PFOS surfactants and have a limited PTFE content range. The other dispersions are PFOS-free and have a wider operating window. The first through third generations will be compared to the new fourth generation dispersion.

Dispersion properties

Information regarding the PTFE dispersions compared and contrasted in this work is provided in Table 1.

It should be noted that the first and second generation PTFE dispersions were plated with lead-stabilized EN chemistry. However, the concentration of lead in the deposit is less than 1000 ppm and is therefore still considered ELV-compliant. Lead-free plating solutions are available and are used commercially with the newer dispersions (G3 and G4). Generations 2 through 4 are commercially available systems (G1 has been discontinued).

The decrease in particle size over the generations has led to an increase in the PTFE that is codeposited. Smaller particle size allows a greater range and flexibility to be achieved. Regardless of particle size, all dispersions discussed in this work are comprised of 60 to 62% PTFE by weight. The particle size was measured in the various PTFE dispersions with a Nicomp Model 370 HPL Submicron Particle Sizer.

Figure 1 provides a comparison of the deposition rates for the different dispersions listed in Table 1 with various amounts of dispersion. The rates are based on EN/PTFE baths at a temperature of 88°C (190°F) and a pH of 4.9 - 5.0. Generations 2 and 4 have

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Table 1

PTFE dispersion parameters

Dispersion	EN Bath	Particle Size, nm	Wt% PTFE Range	PFOS/PFOA-Free
Generation 1 (G1)	Pb-stabilized	<380	1 - 6	No
Generation 2 (G2)	Pb-stabilized	<380	7 - 9	No
Generation 3 (G3)	ELV-compliant	<300	1 - 9	Yes
Generation 4 (G4)	ELV-compliant	<250	1 - 13	Yes

roughly the same deposition rates, 7.1 - 8.4 μm/hr (0.28 - 0.33 mil/hr), which stay consistent over the range of dispersion concentrations. Generation 1 has a slower rate at lower dispersion concentration, but the rate increases with increasing dispersion amounts, to a maximum rate of 8.4 μm/hr (0.33 mil/hr). Generation 3 behaves similarly to G1, but the minimum and maximum rates are 7.6 - 10.9 μm/hr (0.30 - 0.43 mil/hr), respectively.

Test parameters

The PTFE content was calculated at various concentrations and bath ages. A stainless steel panel of known weight (with a sulfamate nickel strike) was plated for one hour in the EN/PTFE bath. Weight gain was recorded and the panel was stripped with 50% HNO_3. A Gooch crucible with a Whatman GF/F filter was weighed and the stripping solution was filtered through it. Subsequent washings and rinsings were also filtered through to assure that all PTFE particles were in the crucible. The crucible was heated for one hour in a 100°C (212°F) oven (or until uniform weight is achieved). The PTFE content was calculated from the panel weight gain and the weight of PTFE from the stripping solution.

Coefficient of friction (C of F; μ) testing was performed with a CSM Instruments NanoScratch Tester by an independent lab. By performing scratch stylus testing with a low constant load and by using a ball instead of the usual diamond-shaped indenter, it is possible to measure the coefficient of friction between two materials without the creation of wear or damage. The constant load was 25 mN over a scratch length of 3.0 mm (0.12 in.). The scratch speed was 3.0 mm/min (0.12 in./min). The stylus was a chromium steel ball with a diameter of 6.0 mm (0.24 in.). Three scratches were made per sample and the average values are presented in this work. All test samples were plated on steel panels. The coating thickness was 6.35 ± 1.27 μm (0.25 ± 0.05 mil). The C of F testing was completed on samples generated from new and aged solutions.

Surface roughness and profiling was accomplished using a ZYGO NewView 200 Interferometer Profilometer and MetroPro PC software. Three scans were made on each sample to give a R_a

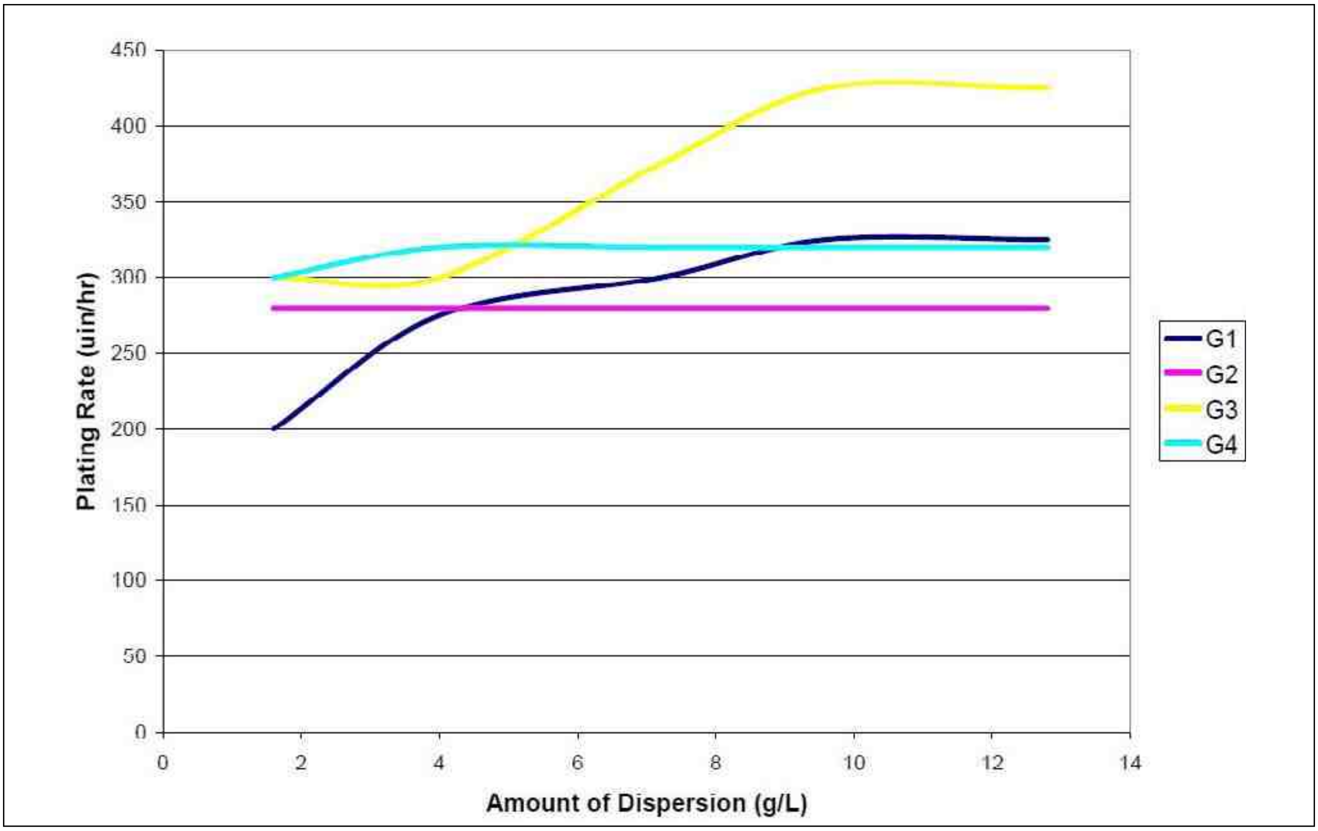

Figure 1—*Comparison of EN/PTFE deposition rates.*

(μ-in) value. R_a is the average roughness of a surface along a scan length.[1] The profilometer used frequency domain analysis (FDA) to generate quantitative 3D images of surfaces. FDA is insensitive to changes in surface characteristics such as color and brightness,[2] which makes it ideal for EN/PTFE coatings, since more PTFE incorporation leads to a darker deposit.

Hardness testing samples were plated on steel panels to a thickness of 63.5 μm (2.5 mil). Samples were tested "as-plated" and after heat-treatment (2 hr at 300°C). A Micromet 5104- V/K hardness tester using a Knoop indenter with a load of 100 g was used. Five indents were made in mounted cross sections from each sample and an average was reported.

A Taber Abraser 5130 with a 1000-g load was used for wear testing. Samples were plated on steel test panels to a thickness of 50.8 μm (2.0 mil). The Taber Wear Index (TWI) was calculated (average mg loss/1000 cycles) after ten 1,000-cycle runs were completed. CS-10 wheels were used and S-11 refacing discs were used between every 1000 cycles.

Results and discussion

PTFE content

The PTFE content test results are given in Fig. 2.

Generation 1 was designed to give higher % PTFE using less dispersion, from 2 to 6 g/L. While G2 was designed to give increasing PTFE using smaller amounts of dispersion for the higher ranges of PTFE incorporation (6 - 9 g/L). These generations were companions, G1 used for the low range and G2 used for the higher range (at least the highest range at the time).[3] For example, with 4 g/L dispersion, G1 gave roughly 18 vol% and G2 gave 10 vol%. On the other hand, at 8 g/L dispersion, G1 gave 22 vol% and G2 gave 27 vol%. These systems worked quite well, provided good deposits, but created an inconvenience for customers who wanted to plate both low and high PTFE deposits. They were required to buy both types of dispersion (and run in separate tanks) or buy one type and use excess dispersion to achieve their required PTFE level. Also, once PFOS/PFOA surfactants were phased-out (2000 to 2002), the raw materials were no longer readily available (from U.S. suppliers). New dispersions had to be created with "greener" intentions in mind.

The more environmentally-friendly Generation 3 was introduced. Generation 3 spans the entire range of PTFE content. Therefore it was possible to use one dispersion for 4 vol% to the highest attainable amount (33 vol%). At 4 and 8 g/L of dispersion, G3 gave results similar to G1. While G3 does not produce 27 vol% PTFE at 8 g/L as G2 does, it has the advantage of reaching higher PTFE levels than either of the two previous systems. Now customers could buy a single dispersion for the entire range of PTFE content from 1 to 9 wt% (4 to 28 vol%).

Generation 4 has the advantage of not only spanning the entire range of PTFE content, but requiring less dispersion to obtain higher PTFE levels and reaching a slightly higher percentage than previously possible. At 4 and 8 g/L dispersion, G4 gives 25% and 33 vol%, respectively. Generation 3 uses 13 g/L of dispersion to obtain an EN/PTFE deposit with 32 vol% PTFE (its highest obtainable level), while G4 uses roughly 10 g/L of dispersion for 35 vol% PTFE deposits. Not only does G4 use 23% less dispersion to obtain its highest PTFE level, it yields 3 vol% higher.

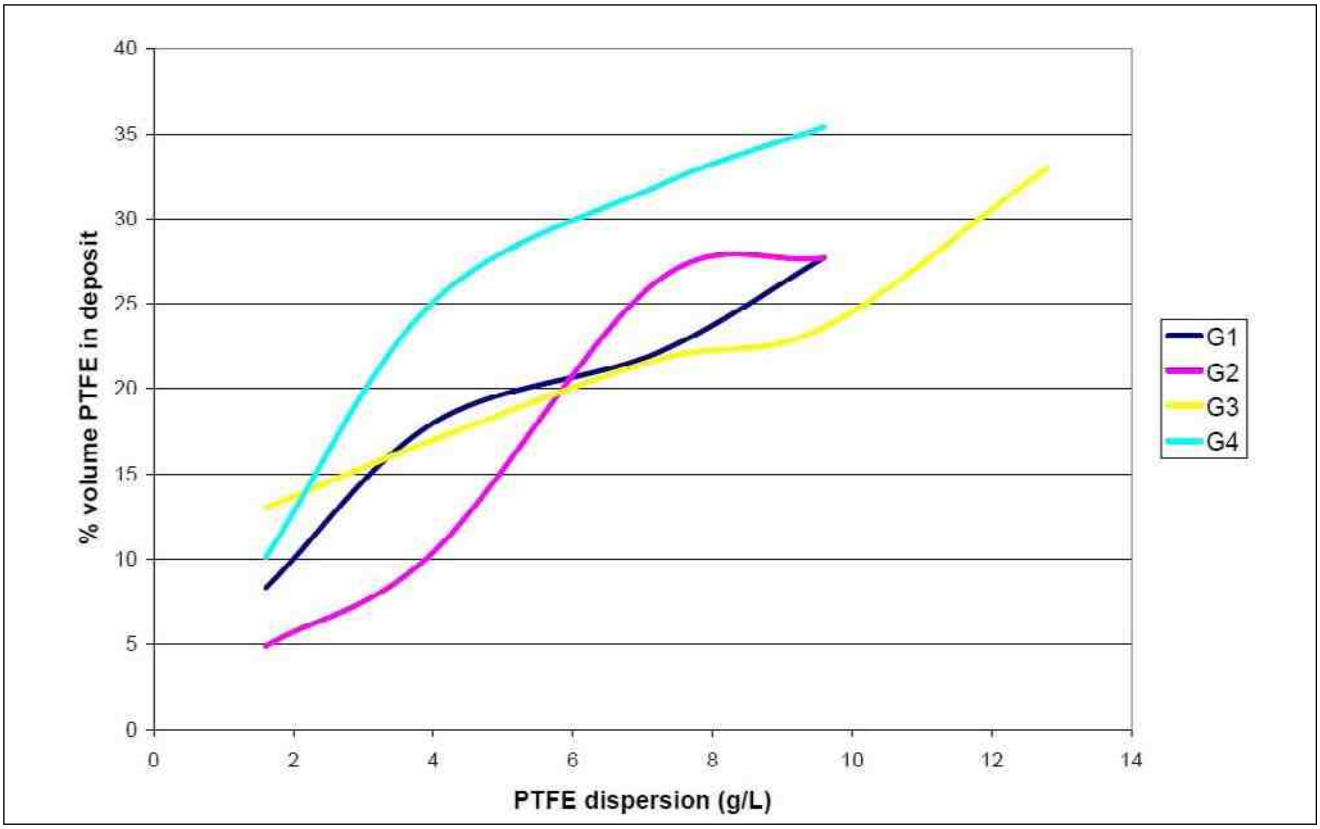

Figure 2—*Amount of PTFE incorporated in the deposit with various concentrations of dispersion mixed into the electroless nickel bath.*

Coefficient of friction

Coefficient of friction results for Generations 3 and 4 are provided in Fig. 3. Overall, the coefficient of friction values decrease with increasing PTFE in the deposit. Generation 4 has a much lower coefficient of friction range for deposits with 2 - 12 wt% PTFE. The minimum C of F value is 0.01 at 12 wt% PTFE. The maximum value is 0.035 at approximately 6.5 wt% PTFE. The lowest and highest C of F value for Generation 3 is 0.05 and 0.08 at 6.5 and 2.0 wt% PFTE, respectively.

Some of the coefficient of friction curves showed measurements that were very close to the detection limit of the instrument. New measurements were completed with a higher load. The original load was 25 mN, so a higher load of 100 mN was chosen. The results changed marginally, for example, with a 25 mN and a 100 mN load the 2.0 wt% PTFE G4 sample had results of 0.024 and 0.043, respectively. A load increase by a factor of four only increased the coefficient of friction by a factor of approximately 1.8.

Typical coefficient of friction values for electroless nickel deposits are much higher. The average mid- and high-phosphorus electroless nickel coatings have a C of F of 0.10 - 0.11 with a 25 mN load. Electroless nickel/ PTFE codeposition reduces the coefficient of friction by a factor of three to four.

Coefficient of friction values have been reported for Generations 1 thru 3 previously.[3] Cylinder and plate wear tests with a 5 N load were used to generate C of F data for G1 thru G3. Direct correlation between those results and the data presented here is not possible. However, the previous results show that G3 produced lower C of F values than either G1 or G2. So it is assumed that, based on those results and the current results for generation 3 and 4, that Generation 4 would have even lower results when compared to G1 and G2.

Surface roughness

The average surface roughness values for deposits from new solutions using Generations 1 thru 4 are presented in Fig. 4. Generation 1 had the highest surface roughness, with R_a values of 16 - 17 μ-in. G1 had a fairly constant roughness over the entire PTFE deposition window. Conversely, G2 started with a lower value of 6 μ-in., reached a peak of 11 μ-in. at 8 g/L dispersion and then the surface roughness fell slightly with dispersion values in the 9 - 12 g/L range. The Generation 3 curve has a unique shape. It provides a higher surface roughness value (higher than G2) from 2 - 7 g/L of dispersion. Then the R_a values fall abruptly from 7 - 9 g/L, and start to level off again between 10 - 13 g/L of dispersion.

Generation 4 has a similar curve to that of G2. It is more linear, with less variation in surface roughness, and not as dependent on the dispersion amount as is G3. G4 starts at a lower R_a value than G3 and dips slightly around 8 g/L of dispersion. Generation 4 has a higher surface roughness from 8 - 13 g/L versus G3. However, G4 achieves its highest PTFE content in the deposit at approximately 9 g/L of dispersion. At this point the G3 and G4 curves intersect at 6 μ-in.

Surface profiling

Surface profiling was completed for the Generation 4 deposits. An example of the results is given in Fig. 5. Contour mapping of EN/PTFE deposit shows a visual representation of the relative smoothness. The profiles shown in Figs. 5a and 5b are of deposits with 7 and 12 wt% PTFE, respectively. The 7 wt% PTFE deposit has a relatively smooth surface, with some small peaks and valleys evident in the upper quadrants. The 12 wt% PTFE profile is much smoother than that of the 7 wt% deposit. What valleys and peaks can be seen are minute and less evident than can be seen in the profile for the 7 wt% PTFE deposit.

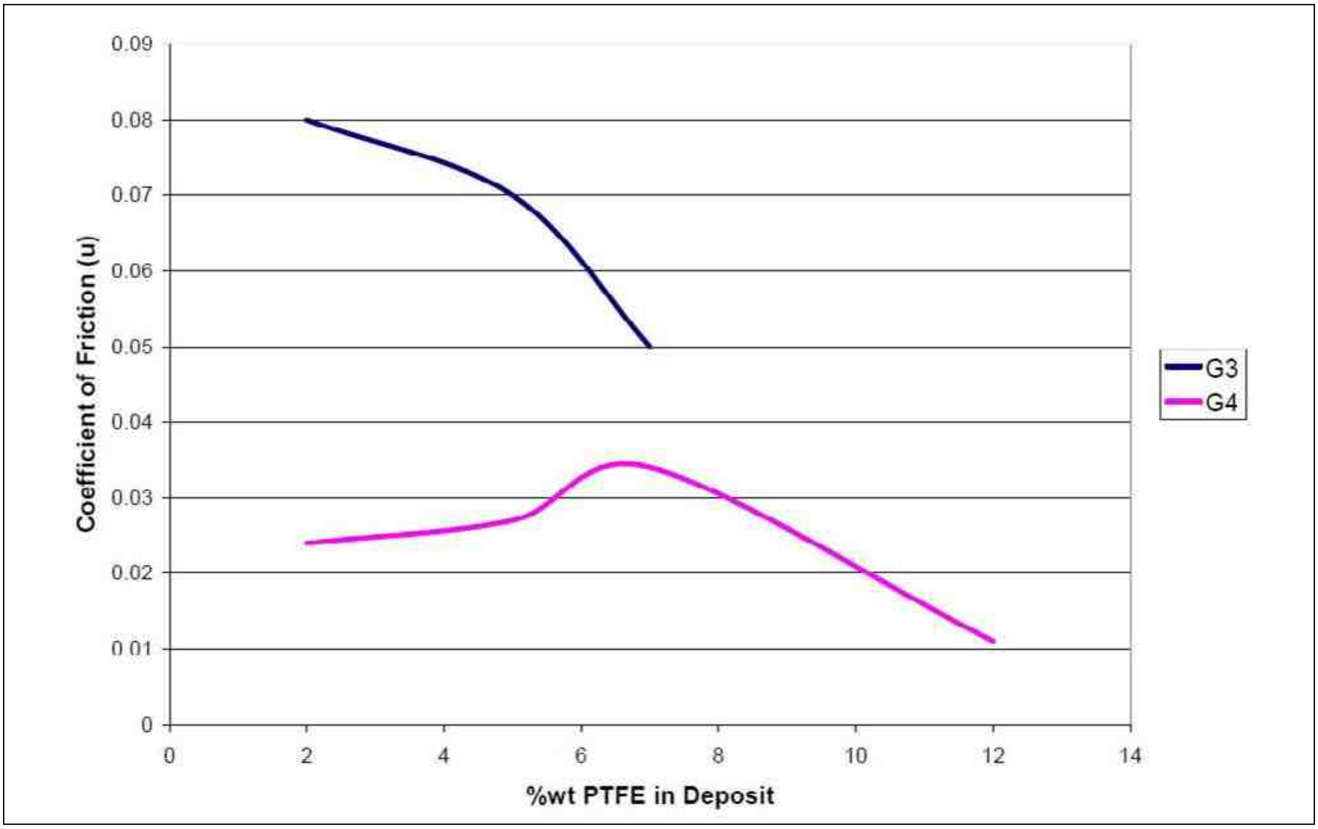

Figure 3—*Coefficient of friction results over 2 to 12 wt% PTFE.*

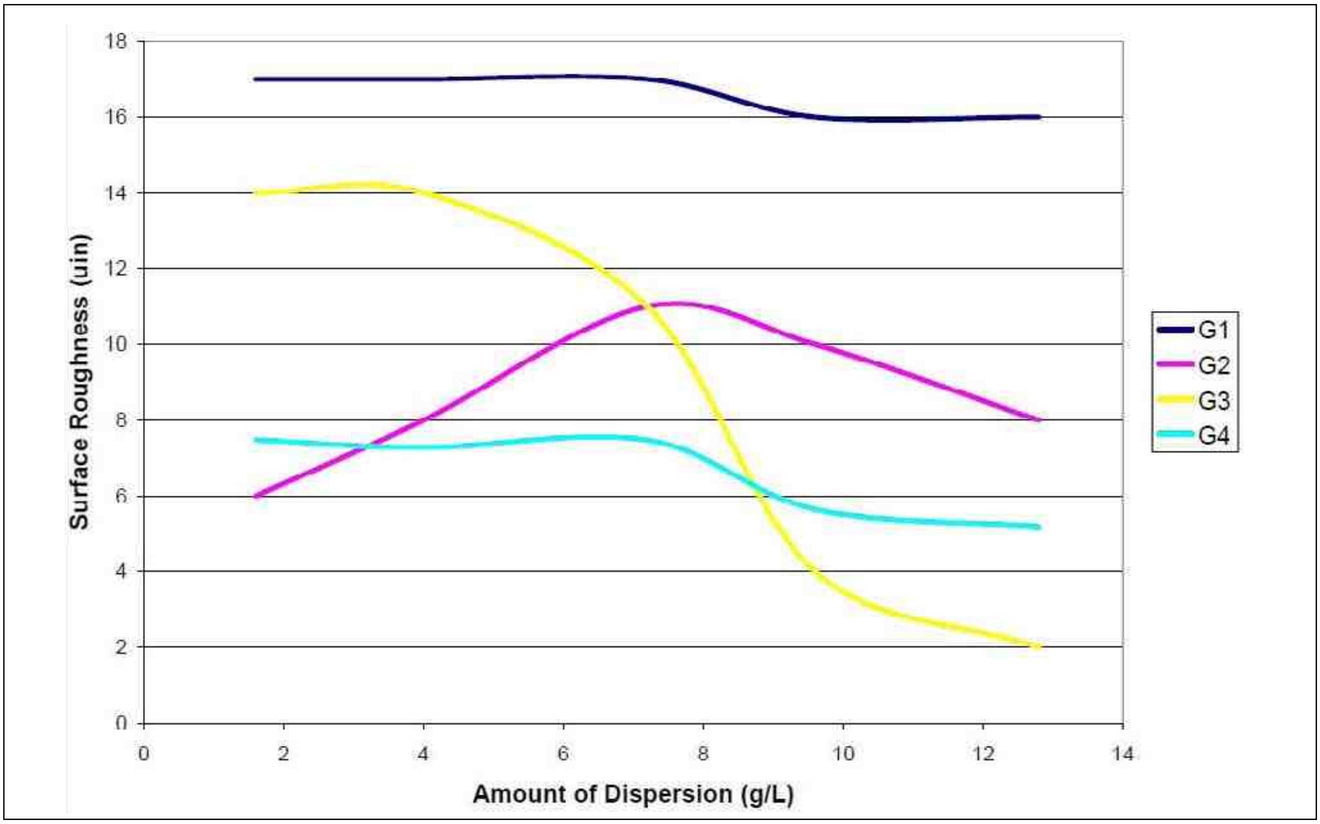

Figure 4—*Surface roughness (R_a) dependency on the amount of PTFE dispersion in the working bath.*

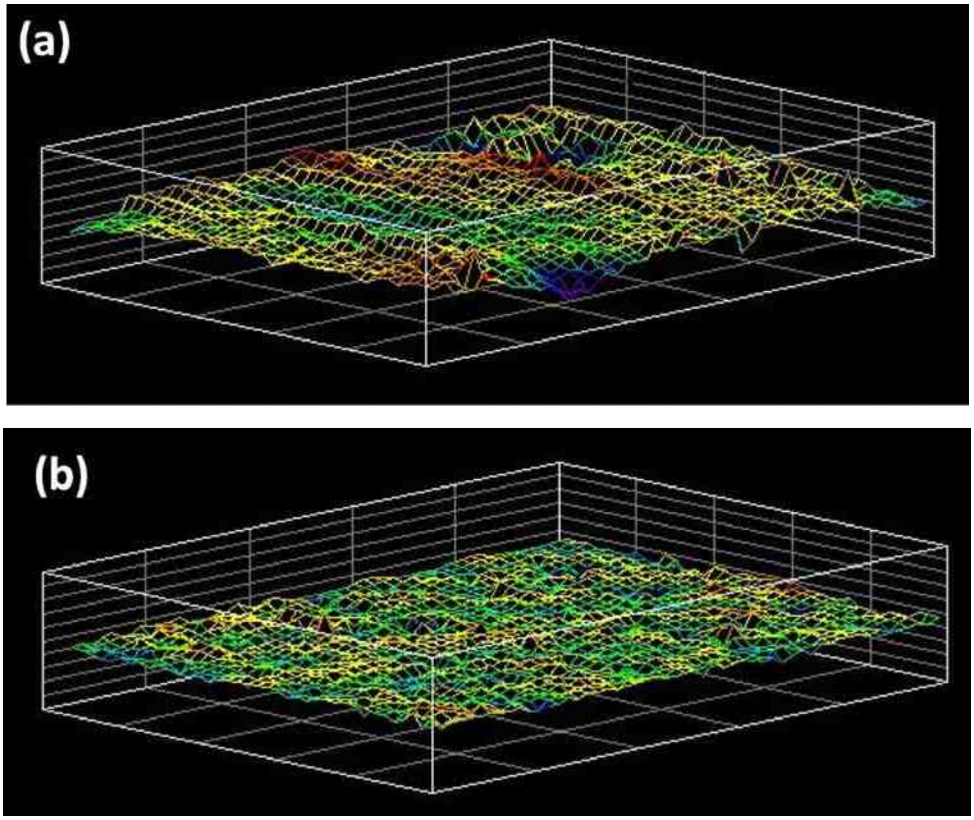

Figure 5—*Surface profiles for (a) 7 wt% PTFE and (b) 12 wt% PTFE.*

The results in Fig. 5 correlate to the coefficient of friction results given in Fig. 3. Generation 4 achieves its highest C of F value at 7 wt% PTFE (0.035) and its lowest value at 12 wt% PTFE (0.012) in the deposit. The same results are shown, in a more visual medium in Fig. 5.

Hardness

The hardness results for Generation 4 are given in Fig. 6. The results are given for Generation 4 only because most EN/PTFE deposits are comprised of approximately 8 - 9 wt% phosphorus and a certain amount of PTFE. The hardness of an EN/PTFE deposit of a similar wt% PTFE (regardless of the PTFE dispersion level), should have a hardness value in the same range, providing that the high-phosphorus electroless nickel is of similar composition and typically generates EN deposits in the 10 - 12 wt% P range (without the PTFE incorporated).

As more PTFE is incorporated into the deposit, the hardness values decrease dramatically. EN/PTFE deposits with small amounts of PTFE incorporated behave more like an electroless nickel deposit. As more and more PTFE is included in the deposit, the more "spongy" and soft it becomes. EN/PTFE deposits are not designed to withstand wear testing with high loadings.

As seen in Fig. 6, heat-treatment increases the hardness. For normal high phosphorus EN, the heat-treatment increases the hardness by approximately 40%. The more PTFE in the deposit, the less effective the heat treatment. For example, the 2.5 and 7.5 wt% PTFE deposits experienced a 25 - 35% increase in hardness after a two-hour bake at 300°C (572°F), while the 12.5 wt% PTFE deposit only showed a 10% increase in hardness after heat treatment.

Wear

The wear resistance of standard high-phosphorus electroless nickel and EN/PTFE deposits with various amounts of PTFE is displayed in Fig. 7. All values are represented as a Taber Wear Index (TWI) value, which is the average milligrams loss per 1000 cycles. This test is designed to show the effect of high loading in wear applications.

The wear increases with increasing incorporation of PTFE particles. Typical high-phosphorus EN has an as-plated TWI of 24, while the as-plated 2.5 wt% PTFE deposit has a TWI of 30. The 5.5, 7.5 and 12.5 wt% PTFE deposits have as-plated TWI values of 54, 89 and 114, respectively. Traditional electroless nickel has better wear resistance after heat treatment, and EN/PTFE deposits share that property. Heat treatment for two hours at 300°C (572°F), reduced the TWI values by 18% for high-phosphorus EN and by an average of 33% for the EN/PTFE deposits.

Conclusion

Current PFOS-free PTFE dispersions are providing a higher quality EN/PTFE deposit with superior properties. Also, the PFOS-free dispersions are environmentally-friendly when compared with the previous generations of dispersions (notably versions 1 and 2 in this work). Versions 3 and 4 can be used for a broad range of PTFE deposit contents. A single dispersion can be used for 1 - 12 wt% PTFE. Previously, two dispersions were utilized - one for lower and one for higher PTFE content ranges. Smaller particle sizes allow for more PTFE particles to be incorporated into the deposit which increases the wt% PTFE and/or allows a more efficient use of the PTFE in the dispersion. Higher PTFE deposits can be achieved

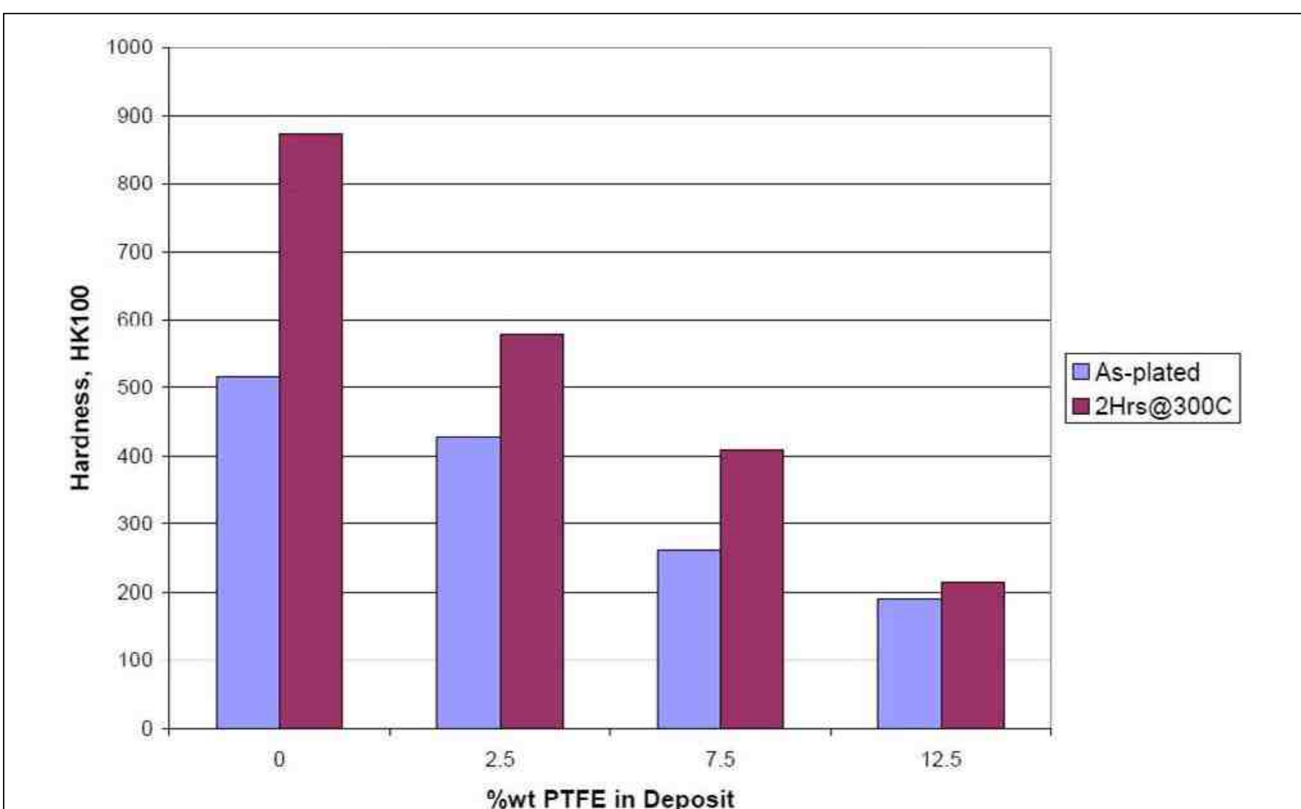

Figure 6—*Hardness of Generation 4 deposits with various amounts of PTFE (wt%).*

with the PFOS-free dispersions. Generation 4 can consistently achieve 3 wt% PTFE more than Generation 3 and use less dispersion to reach its maximum of 12 wt%. The PFOS-free dispersions also exhibit lower coefficient of friction and surface roughness values when compared to Generations 1 and 2.

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References

1. ASME B46.1 - 2002, "Surface Texture (Surface Roughness, Waviness and Lay): An American National Standard," American Society of Mechanical Engineers, New York, NY, 2002.
2. R&D Technical Bulletin, "What is Frequency Domain Analysis?," ZYGO Corporation, Middlefield, CT, September 1993; http://www.zygo.com/library/papers/wifda.pdf (last accessed 10/17/09).
3. D. Crotty & D. Beckett, "Properties of Electroless Nickel/PTFE Deposits with New Wetting Agents," in *Proc. AESF SUR/FIN 2004*, NASF, Washington, DC; p. 168.

About the author

Nicole Micyus is a R&D Chemist with MacDermid's worldwide engineering coatings research team. She started with MacDermid in 2005 at their New Hudson, Michigan technical center. Since then she has worked on EN formulations and mechanical/physical testing of electroless nickel coatings. In early 2008, Nicole took over responsibility for EN/PTFE codeposition research and development. She received her Master's degree in Chemistry from Oakland University and her Bachelor's degree from GMI Engineering & Management Institute.

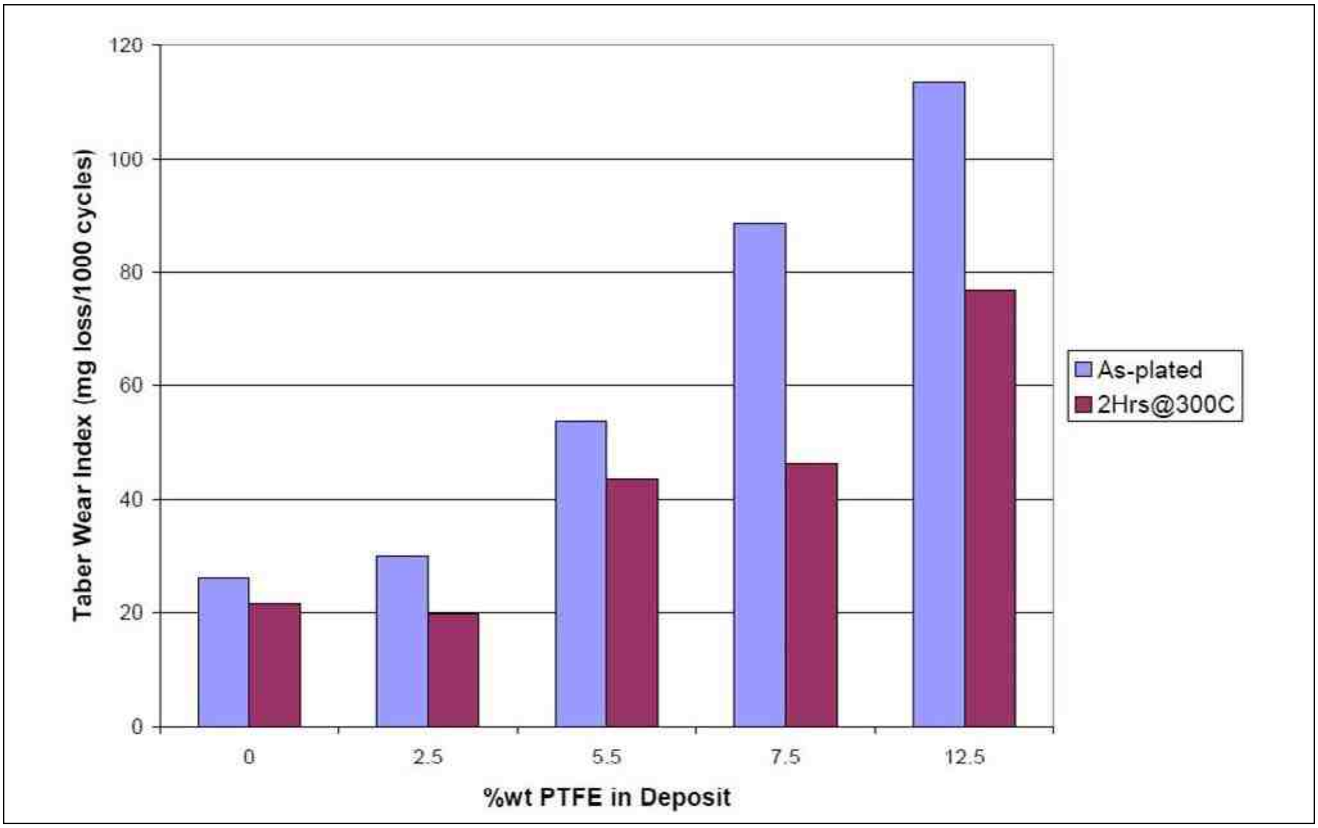

Figure 7—*Taber Wear Index of EN/PTFE deposits.*