Properties of Electroless Nickel/PTFE Deposits with New Wetting Agents

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The obsolescence of certain raw materials in the chemical industry that were used for PTFE dispersions has prompted considerable R&D work to replace these materials. Several potentially important PTFE dispersions have been developed as a result of this work. This paper will discuss the properties of deposits plated from electroless nickel/PTFE processes. The properties discussed will include deposition characteristics of the processes and studies of wear properties and surface roughness of the deposits as affected by PTFE content in the deposits.

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Introduction

The electroless nickel/PTFE deposit is a one in which PTFE particles are uniformly co-deposited with the nickel phosphorous as deposition occurs. This deposit type has been used extensively to provide lubrication for friction and wear applications. In addition, the deposit has been used to facilitate mold release for a range of plastic and rubber products. The PTFE deposit is just one example of a range of co-deposits. Silicon carbide, diamonds, boron nitride, polyfluorinated graphite and other particles are also used to form co-deposits in the electroless nickel matrix.

Early descriptions of the process were provided by Brown [1] and Helle [2]. The PTFE particles are usually dispersed in a concentrate with the help of suitable wetting agents. This dispersion concentrate is then added to an electroless nickel plating bath. When the article to be plated is immersed in the plating bath the deposition process proceeds to build the nickel phosphorous coating where the PTFE particles become uniformly co-deposited throughout the deposit. The PTFE process is somewhat unique, when compared with other particle co-deposition processes, in that the PTFE particle is suspended as an emulsion in the plating bath. The PTFE particle is attracted to the plating surface by a charge provided by the wetting agents, and thus becomes incorporated into the deposit. Most of the other particle types are essentially suspended in solution by agitation and become trapped in the deposit when they happen to fall by gravity onto the plating surface. Some of the wetting agents commonly used to prepare the PTFE dispersions have been found to have suspected environmental and health problems resulting in the discontinuation of these materials by the manufacturers. As a result a new class of dispersions has been developed to fill this void using currently available materials.

The wear properties of the EN/PTFE deposits have been extensively investigated. Parker [3] reported ring and block wear results for EN/PTFE as part of a larger study of EN deposits. Dennis [4] reported results of pin and disk tests. Tulsi and Hadley [5,6] reported results of pin and plate, block and ring and cross cylinder wear tests. Ebdon [7, 8, 9, 10] reported a series of tests using a reciprocating cylinder and plate method. Duncan [11] provided a study of Tabor wear of EN/PTFE deposits. Roberto [12] reported a study of cross cylinder wear results were the two cylinders were coated with combinations of EN or EN/PTFE. Sakamoto [13] reported studies using the pin and disk and the plate and ball wear tests. Nishira [14] reported a study using a rotating disk and alumina ball.
Finally, Pena-Munoz [15] reported wear results from a pin and disk method.

Of these only the report from Nishira [14] tested a wider range of PTFE content in the deposits. In today's market, specifications have been provided by OEMs for a wide range of PTFE content from 3-30% v/v. We saw a need to look at this wider range of deposits. We chose to test this wider range of deposits with the cylinder and plate method using the same instrument used for earlier reports. This paper describes the preparation of the range of deposits, some deposit properties and the wear results from the cylinder and plate tests. The results will also provide a comparison of the new and old dispersion types.

Deposit Preparation

Three different dispersion concentrates were used in this work that will be called TF, N, and I [16]. The TF and N dispersions are long term commercial products using wetting agents that have been discontinued by the manufacturers. The TF dispersion is designed to provide about 6-15% v/v of PTFE. The N dispersion is designed to provide about 18-25% v/v of PTFE. Both dispersion types are capable of higher PTFE deposits when the plating bath is fresh. The I dispersion was recently developed using modern commercially available wetting agents. The I dispersion is capable of providing 6-25% v/v PTFE in the deposit. Each of the three product dispersion concentrates contains 60% w/w of PTFE.

The plating baths were all made up using the same electroless nickel process [17]. Various amounts of the dispersion concentrates were used to obtain the desired range of PTFE in the deposits. The baths were operated at 86-90°C, pH 4.9-5.2 and with very mild solution agitation. The sample plates were plated with companion plates. The extra companion plates were measured periodically during the plating process until the desired thickness of 12-14 um was achieved. Table I summarizes the deposition and deposit properties of the sample plates.

Table I
Deposit and Deposition Properties

Sample	Type	Disp. Used mL/L	Rate um/hr	PTFE wt %	PTFE Vol. %	Roughness Ra um
1	TF	1	7.9	1.1	4.1	2.17
2	TF	2	7.9	4.0	14.3	1.91
3	TF	3.5	7.9	6.3	21.2	1.89
4	TF	5	7.9	7.4	24.2	1.85
5	TF	7	7.9	8.0	25.8	1.85
12	N	6	8.9	8.7	27.6	1.96
13	N	8	11.5	10.9	32.9	1.91
6	I	1	5.9	1.8	6.8	2.17
7	I	3.5	8.3	5.2	18.0	1.85
8	I	7	11.2	6.9	22.9	1.57
9	I	10	13.8	7.5	24.5	1.81

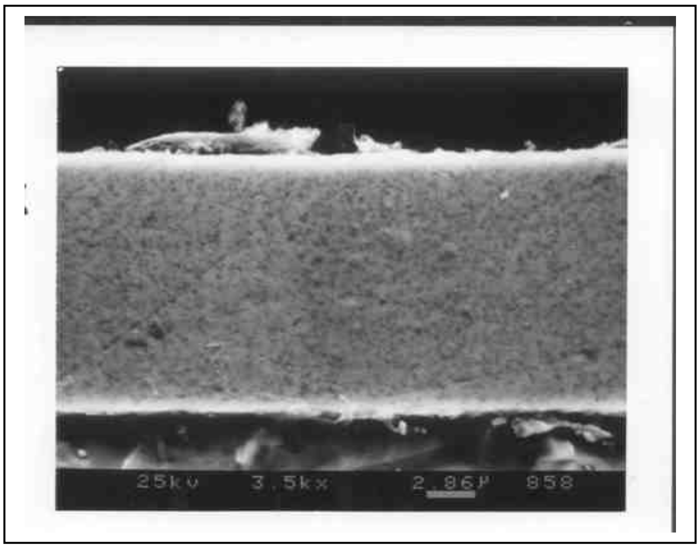
Note: The surface roughness Ra of the unplated plates averages 1.69 um.

The % v/v of PTFE in the deposits is calculated from the measured [16] % w/w, the density of the PTFE material and the density of the NiP electroless nickel deposit. The NiP deposits are approximately 9.0% w/w phosphorous [18] with a density of about 8.0 g/cm^3. The PTFE powder is reported to have a density of about 2.1 g/cm^3. The equation for this conversion is presented with equation 1.

$$\% \text{ v/v} = \frac{(\%\text{w/w}) / d_{PTFE}}{(\%\text{ w/w})/d_{PTFE} + (1-\%\text{w/w})/d_{NiP}} \quad (1)$$

Figure 1 shows a cross section photomicrograph of a deposit with about 24% v/v PTFE in an electroless NiP deposit prepared using the I type dispersion.

Figure 1
Photomicrograph of 24% v/v PTFE Deposit Cross Section. 3500X



Cylinder and Plate Wear Tests

The wear tests for this study were obtained on the Cameron-Plint Tribology High Frequency Friction Machine. Photographs of the instrument are provided in Appendix I. This is reported to have been the same instrument used to develop results reported in the 1980's [7,8,9,10]. The moving work piece was a 1 cm diameter steel cylinder that was polished and cleaned for each test. The test plate was mounted in the fixture and the cylinder was placed on top of the plated surface. The cylinder was loaded by the instrument to the desired force. For most tests a force of 5 newtons (N) (approximately 500 grams) was used, but a few tests were run at 7 and 10 newtons. The instrument was set to move the cylinder at 10 Hz over a 2 cm path and most tests were run 30 minutes. If the deposit had failed before 30 minute time then the test was sometimes ended. All tests were run without any additional lubricant other than that provided by the EN/PTFE deposits.

The wear results for the dispersion types TF and N prepared with obsolete wetting agents, are presented in Table II. Figure 2 illustrates the friction wear curves for the tests of dispersion types TF and N. The table shows the apparent coefficient of friction as the deposit is worn by the reciprocating cylinder. The changing coefficient of friction is a measure of the wear between the surfaces. Also noted in the table is the chatter point. This is the time at which the movement of the cylinder becomes noisy as evidenced by the vibration of the chart pen as well as an audible noise. This is a measure of the point where the unlubricated metal against metal movement begins.

Table II
Coefficient of Friction Measurements for Dispersion Types TF and N

Sample	1 TF	2 TF	3 TF	4 TF	5 TF	12 N	13 N
% v/v PTFE	4.1	14.3	21.2	24.2	27.6	27.6	32.9
Load	5 N	5 N	5 N	5 N	5 N	5 N	5 N
	Coefficient of Friction						
0 min	0.06	0.10	0.04	0.04	0.10	0.08	0.00
1 min	0.06	0.12	0.04	0.04	0.12	0.08	0.00
5 min	0.08	0.22	0.08	0.05	0.12	0.10	0.00
10 min	0.16	0.28	0.08	0.05	0.16	0.10	0.00
15 min	0.26	0.52	0.10	0.08	0.20	0.10	0.00
20 min		0.52	0.12	0.08	0.24	0.10	0.00
25 min			0.13	0.08	0.28	0.10	0.00
30 min				0.08	0.32	0.10	0.00
Chatter	6 min	10 min	16 min	>30 min	>30 min	>30 min	>30 min

Note: The Coefficient of Friction for Sample 13 was not zero but was too low to measure.

The wear results for dispersion type I, made with currently available materials, are listed in Table III. Similarly, Figure 3 illustrates the wear behavior of the deposits made using dispersion type I.

Table III
Coefficient of Friction Measurement for Dispersion Type I
And Normal Electroless Nickel for Comparison

Sample	EN	6 I	7 I	8 I	9 I
% v/v PTFE	0.0%	6.8	18.0	22.9	24.5
Load	5N	5 N	5 N	5 N	5 N
	Coefficient of Friction				
0 min	0.10	0.08	0.04	0.04	0.04
1 min	0.10	0.16	0.08	0.04	0.02
5 min	0.10	0.16	0.12	0.06	0.02
10 min		0.18	0.14	0.08	0.00
15 min			0.18	0.12	0.02
20 min			0.20	0.14	0.04
25 min				0.16	0.04
30 min				0.16	0.04
Chatter	1 min	1 min	20 min	>30 min	>30 min

For comparison, a plate with normal electroless nickel was also tested at a load of 5N. The as plated deposit showed a coefficient of friction of 0.10 but the steel to electroless nickel contact was noisy from the start. The electroless nickel deposits tend to have a low coefficient of friction but wear between steel and EN can be noisy without lubrication. The results of this test, run for 5 minutes, are shown in Table III.

Figure 2

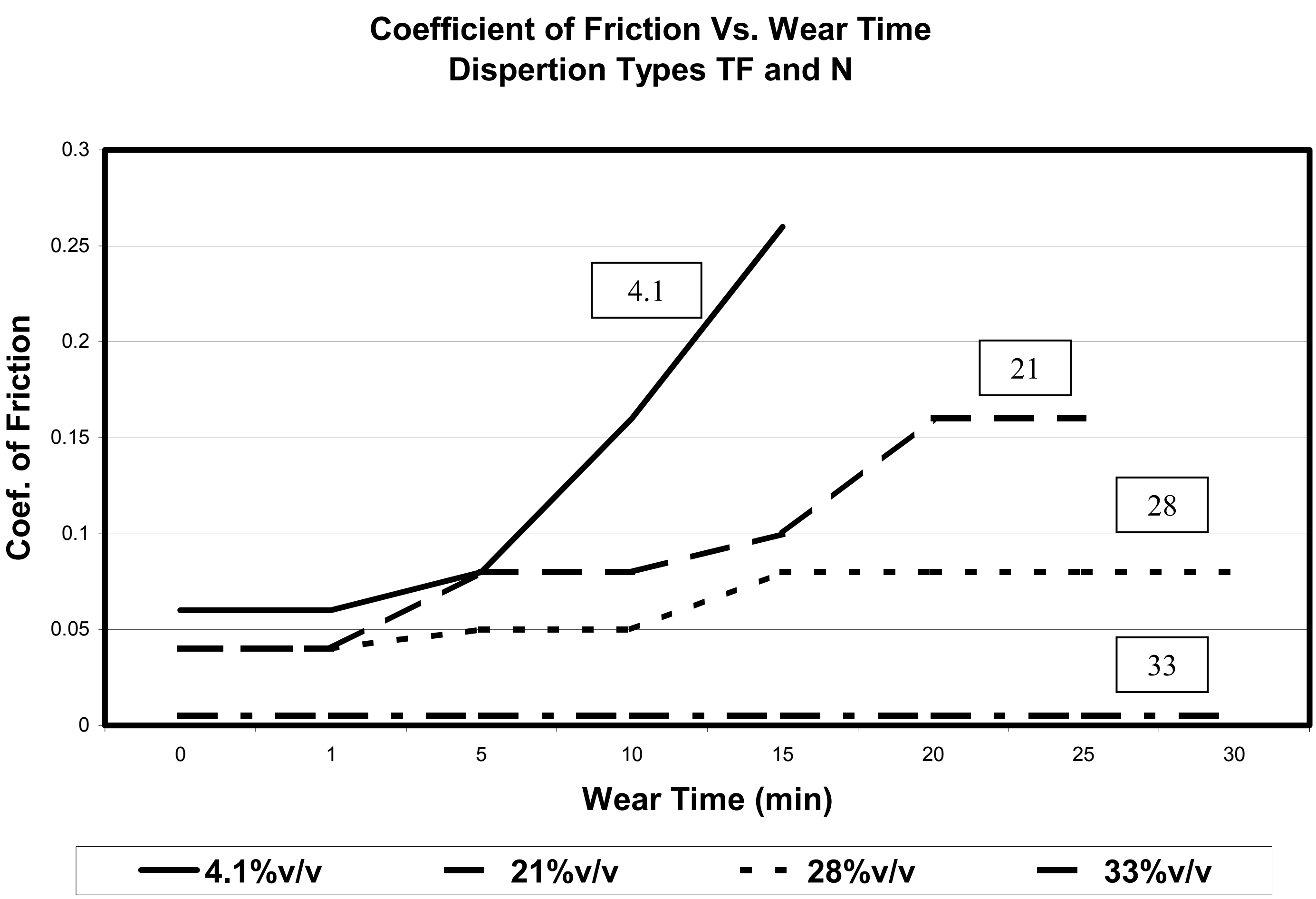
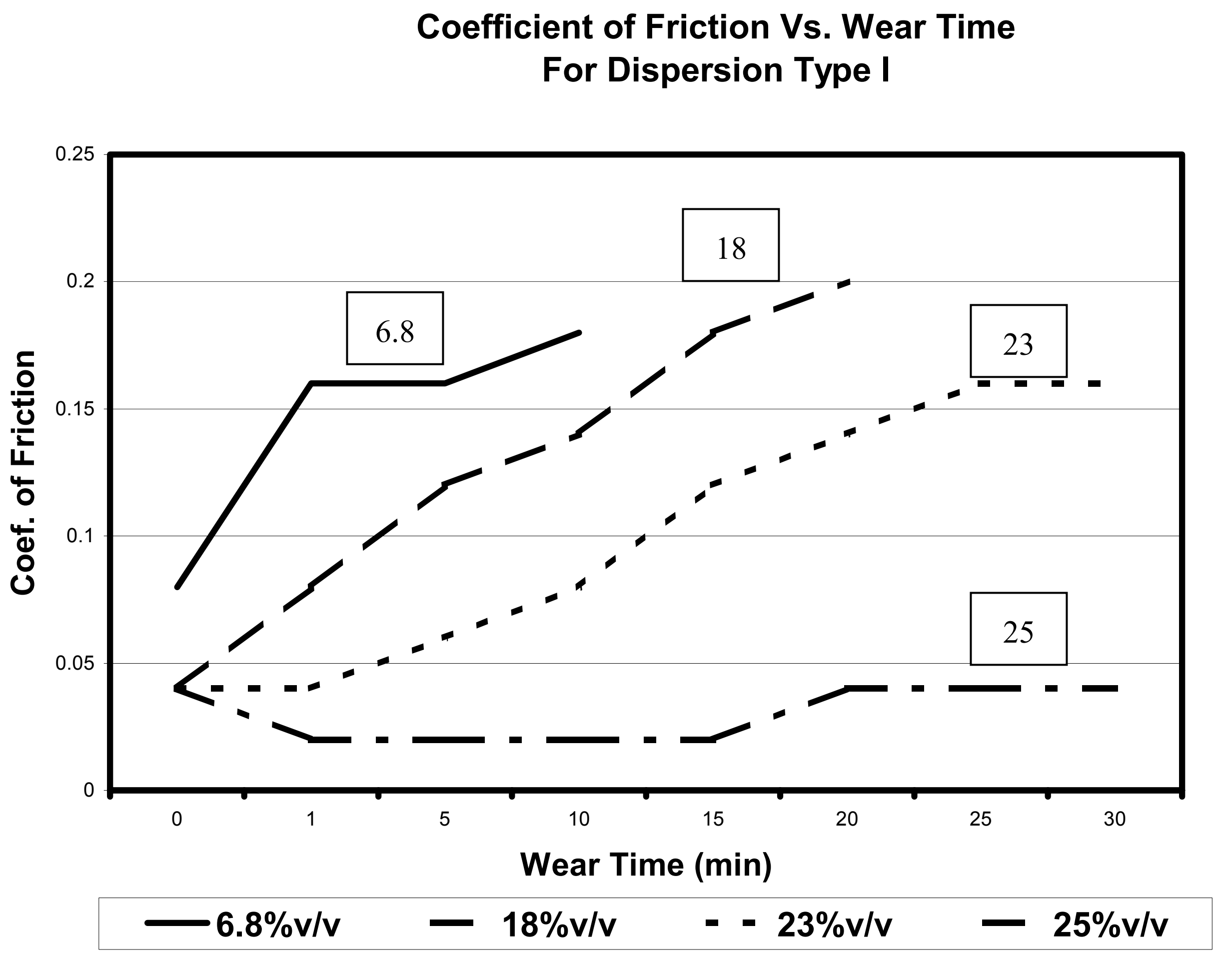


Figure 3



Two of the deposits, with 24.2 and 32.9% v/v of PTFE, were chosen to be tested at loads of 5, 7 and 10 newtons. The results of this series are presented in Table IV.

Table IV
Variable Load for Deposits at 24.2 and 32.9% v/v PTFE

Load (N)	Coef. Friction	Chatter Point (min)	Coef. Friction @ Chatter Point
24.2% v/v PTFE			
5 N	0.04	>30 min	0.04 @ 30min
7 N	0.04	>30 min	0.04 @ 30 min
10 N	0.06	5 min	0.12
32.9% v/v PTFE			
5 N	0.0	>30 min	0.0 @ 30min
7 N	0.03	>30 min	0.0 @ 30min
10 N	0.04	>30 min	0.05 @ 30min

Note: Where the coefficient of friction is tabulated as zero the result was too low to measure.

The data in Tables II, III and IV show that some of the deposits, generally those with low % v/v of PTFE, wear through and begin to chatter before 30 minutes of testing is complete. Figure 2 illustrates some of this data for dispersion types TF and N and Figure 3 illustrates the data for dispersion type I. The deposits with more PTFE tend to remain quiet through the 30 minute duration of the tests. However, in all cases the deposit is eventually worn though to the steel substrate at the end of the test. The deposits with higher PTFE content apparently have enough PTFE to lubricate the mating surfaces. Photomicrographs of the wear areas on the sample plates have been prepared to study this issue. The plates themselves have a rough surface as evidenced by the Ra of 1.69 um. Figure 4 is a photomicrograph of a typical plated surface to illustrate this roughness.

Figures 5, 6, and 7 show the same 24.2% v/v deposit that has been worn at 5, 7, and 10N respectively for 30 minutes. Table IV shows that the test run at 5 N did not chatter during the 30 minute test resulting in Figure 5 which shows that little of the panel's natural roughness has been worn away.

The panel tested at 7N for 30 minutes, Figure 6, continued quietly for the full 30 minutes. There is some wear noted to the panel's natural roughness.

The panel run at 10N for 30 minutes began to chatter after 5 minutes but the test was allowed to continue. Figure 7 shows that the continued poorly lubricated action wore the panel's natural roughness away completely, actually making the panel surface very smooth.

The photomicrographs of the 32.9% v/v deposit show that the 30 minutes of quiet wear at 5, 7 and 10 newtons broke though the deposit but did not cause complete wear of the natural panel roughness. Figure 8 shows the 32.9% v/v deposit tested at 10N with little damage to the steel substrate.

Figure 4
Photomicrograph of the EN/PTFE surface showing Surface Roughness of Steel Base. 50X

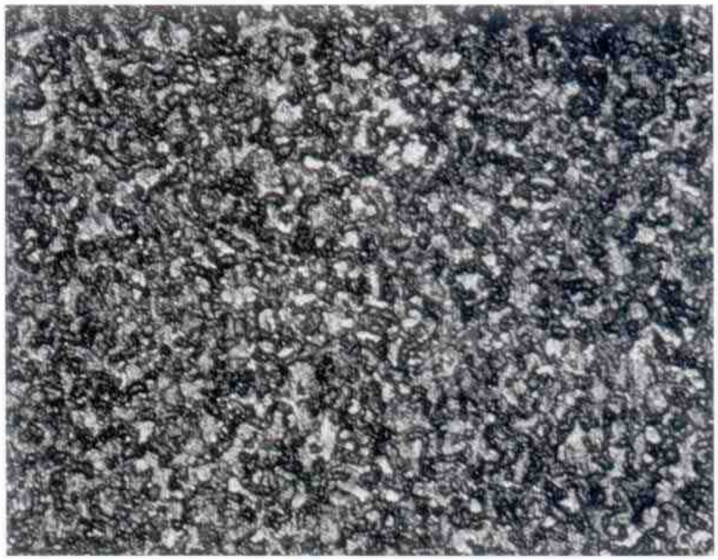


Figure 5
Photomicrograph of a 24.2% v/v EN/PTFE Deposit tested at 5N. 50X

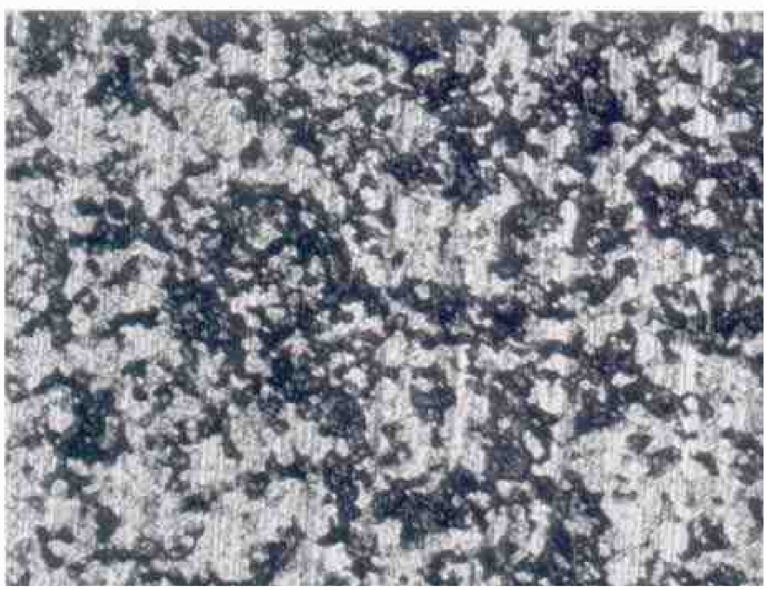


Figure 6
Photomicrograph of a 24.2%v/v EN/PTFE
Deposit Tested at 7N. 50X

Figure 7
Photomicrograph of a 24.2% v/v EN/PTFE
Deposit Tested at 10N. 50X

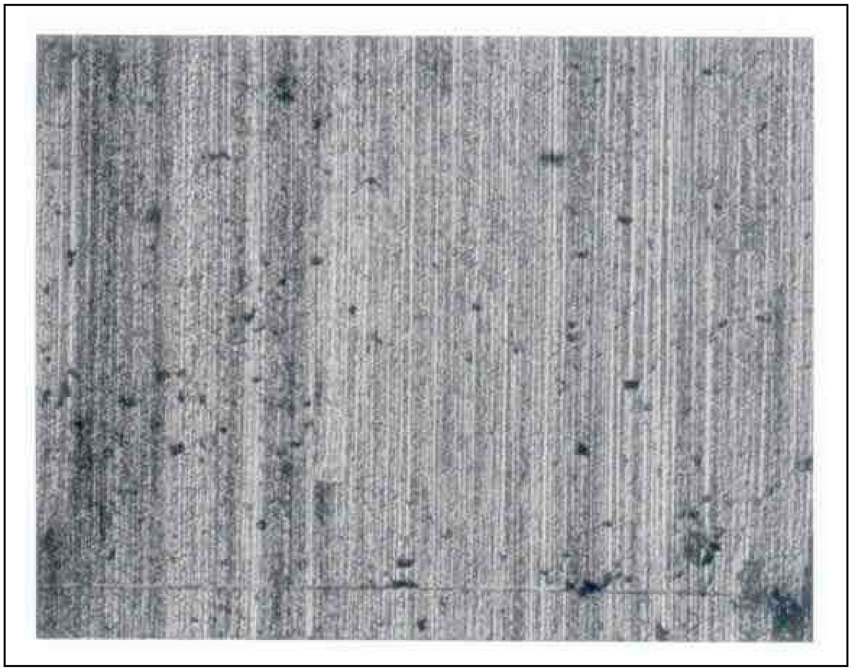
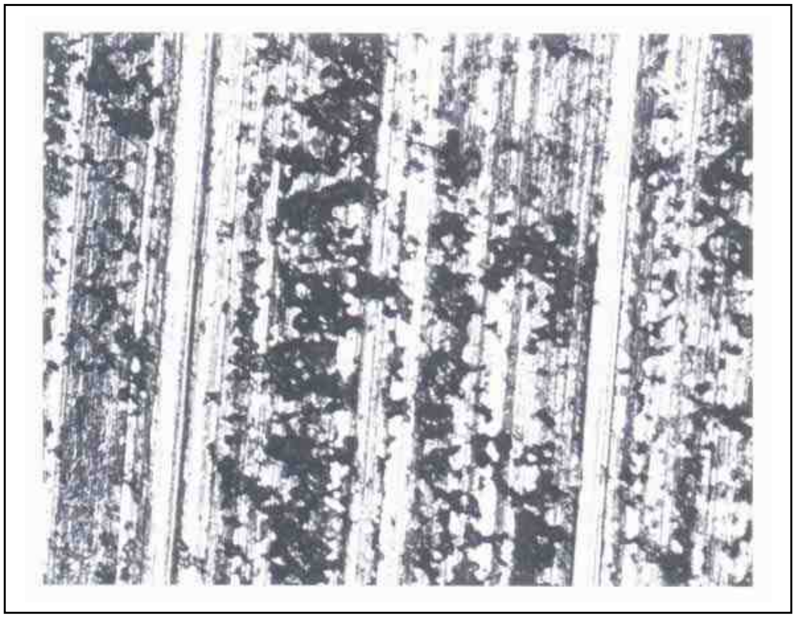


Figure 8
Photomicrograph of a 32.9% v/v EN/PTFE
Deposit Tested at 10N. 50X



Summary

- This study provides a view of the wear properties of the EN/PTFE deposit over a wide range of PTFE content in the deposit. The industry actually specifies deposits over this range for many applications.

- The data presented in Table I show that the old and new types of PTFE dispersion provide for the desired range of PTFE content in the deposits. However, the new dispersion type I tends to provide a faster plating rate when compared with the older types. The deposit surface roughness, Ra, is also similar for the new and old dispersion types.

- Tables II and III present the wear data. Both tables show that if the PTFE content in the deposit is low the starting coefficient of friction is low but the steel cylinder wears though the deposit rather quickly and the contact becomes noisy. As the PTFE content in the deposit is increased the sliding contact remains quiet longer. If the PTFE content is high enough the contact remains quiet even though the deposit may have been worn through. In these cases, enough PTFE remains between the surfaces to lubricate the sliding surfaces.

- The EN/PTFE deposit is a soft deposit so that it cannot tolerate high loads. Table IV shows that a higher load can be tolerated if the PTFE content is high enough to provide sufficient lubrication with this type of friction wear test method.

- The photomicrographs of worn surfaces have been provided to show that if the PTFE content is high enough there is some protection from wear even if the EN/PTFE coating has been worn through to the base metal.

- For comparison, an normal electroless nickel panel was also tested for wear. The coefficient of friction between the EN to steel surfaces was low but the metal to metal action was noisy without lubrication.

Acknowledgements
The authors wish to acknowledge the support of MacDermid Inc. in this work and also wish to acknowledge the assistance of Paul Bray, an area sales manager with MacDermid Inc. in Leeds, UK. Also, we wish to thank Surface Technology plc of Leeds, UK for the generous access to the Cameron-Plint Tribology instrument in their laboratories.

References
1. Brown, H., US Patent 3,677,907 (1972).
2. Helle, K., Kamp, A., US Patent 4160,707 (1979) and Helle, K., Groot, R., US Patent 4,302,374 (1981).
3. Parker, K., *Plat. & Surf. Fin.,* **61**(9), 838 (1974).
4. Dennis, J., et al., *Trans. IMF***, 59**(4), 118 (1981).
5. Tulsi, S., *Trans. IMF***, 61**, 147 (1983).
6. Hadley, J., Tulsi, S., *Proc. AES 71th Tech. Conf.* 1984, Paper B-4.
7. Ebdon, P., *Int. J. Veh. Design, JAVD Congress on Veh. Design and Comp*. 1985 Paper B16.
8. Ebdon, P., *Int. J. Materials and Product Tech*., **1**(2), 290 (1986).
9. Ebdon, P., *SAE Conf.,* Paper 880875, April 4-7, 1988.
10. Ebdon, P., *Plat. & Surf. Fin.***, 75**(9),65 (1988).
11. Duncan, R., *Plat. & Surf. Fin.,* **76**, 33 (1989).
12. Roberto, O., *Surface Modification Technologies II*, Sudarshan T.S. ed, The Minerals, Metals & Materials Soc., 1989.
13. Sakamoto, T. et al**.,** *Proc. Jap. Int. Tribology Conf***.,** Nagoya 1990.
14. Nishira, M., Takano, O., *Plat. & Surf. Fin.,* **81**(1), 48 (1994).
15. Pena-Munoz, E., et al., *Surface and Coatings Tech***., 107**, 85 (1998).
16. Elnic 121TF, Niklad Ni-Lon, Niklad ICE Technical Data Sheets, MacDermid, Inc., 245 Freight St., Waterbury, CT 06702.
17. Elnic 101 Technical Data Sheet, MacDermid, Inc., 245 Freight St. Waterbury, CT 06702.
18. Parkinson, R., *Properties and Applications of Electroless Nickel*, Series 10081, Nickel Development Institute Series, Toronto, 1997.

Appendix I
Cameron-Plint Tribology High Frequency Friction Machine

View showing motor, load gauge and open sample cell.

View showing sample cell with test plate and cylinder.

Control Panel with oscilloscope, power controls and chart recorder.