CMP FORMULATIONS FOR THE USE ON NICKEL-PHOSPHORUS ALLOYS

Technical Field of the Invention

This invention relates to CMP ("chemical mechanical planarization") materials and specifically to CMP materials for use in treating nickel-phosphorous alloys. The specific alloys targeted by the present invention are known as high-phosphorus alloys and contain 9 to 12 wt% of phosphorous. Such alloys are conventionally deposited via an auto catalytic nickel plating process, typically called electroless nickel plating. Specifically in the manufacture of hard disks for hard-disk-drives (memory storage media), said nickel-phosphorous alloys are deposited on an aluminum substrate.

Background of the Invention

To manufacture hard disk drives, certain processes require an electroless nickel-plated substrate to demonstrate a highly planar surface. "Planarity" is quantified through the measurement of "waviness", "flatness" and "roughness". In addition to planarity, certain criteria determine the further processing of post electroless nickel-plated, aluminum substrates. In totality, these criteria are "waviness", "roughness", "outer diameter curvature", "flatness" and surface defects. Waviness, roughness, outer diameter curvature and flatness are to be at a minimum in this context. Surface defects such as "pits", "bumps" and "scratches" are defined by any disruption in the nickel-phosphorous lattice, which has a depth or height greater than or equal to twelve angstroms. In addition to seeking a planar surface that is void of surface defects, the CMP process of nickel-phosphorous plated, aluminum substrates must be accomplished in an efficient manner with respect to cycle time and labor intensity.

Currently available CMP formulations have not succeeded in removing a Ni-P layer at an adequate rate when using abrasive particles consistent with achieving an adequately planar surface. In practical terms this means abrasive particle sizes of from 15 to 120 nanometers. As a result the tendency has been to use abrasives with a larger particle size to reduce the mean distance from "peaks" to "valleys" across the nickel-phosphorous surface very rapidly and follow with a process using particles with a range from 15-120nm to create a "fine" finish with respect to planarity and surface defects. A "fine" finish is defined by the optimum surface condition available to this specific process.

The CMP formulation of this invention is specifically designed to create a surface on a nickel-phosphorous layer that is suitable in all respects for further operations in the fabrication of a superior electronic component. Specifically it is capable of producing a highly uniform, minimum waviness surface in a one-step operation. It does this by using a CMP formulation that greatly increases the material-removal effectiveness of abrasives with particle sizes more usually associated with the later polishing operation.

Normally in this context the CMP surface-generating process is accomplished in two operations: a first involving aggressive material removal until an approximate level is achieved and thereafter a more gentle process in which the desired surface finish, in terms of low surface roughness and micro-waviness, is pursued. The solutions used in the first polishing stage are frequently comprised of abrasive particles, (usually of alumina), with a particle size of from about 0.3 to 0.44 micrometers, and a

chemical accelerant. The second action is a planarization action in which the surface defects created by the first material removal action are removed and a surface with an acceptable pre-determined smoothness and minimal waviness is created. This second stage of polishing is typically accomplished, using a finer abrasive (colloidal silica) and a chemical accelerant, in the presence of an oxidizer.

The two sequential operations can take a substantial amount of time and are labor intensive. As a two-step process also requires more handling of the substrates surface defects are commonly introduced by human handling and transport of the product. It is therefore desired to fabricate a process where a substrate is properly processed via CMP in one step and on a single piece of equipment. A suitable formulation meeting these criteria has now been devised which can be used on a nickel/phosphorus alloy surface to create a finish equivalent to that obtained using a conventional two-stage process, in the same as or reduced time frame.

General Description of the Invention

The present invention provides a CMP formulation for the treatment of a nickel/phosphorus alloy which comprises a dispersion of abrasive particles with particle sizes from 15 to 80 nanometers and selected from the group consisting of silica, alumina, titania, ceria, zirconia and mixtures thereof dispersed in a formulation having a pH of from 2.4 to 2.6 comprising:

a. an oxidizer;

b. a chemical accelerant comprised of four groups:

(1) a phosphonate

(2) a carboxylic acid

(3) a phosphate or phosphite

(4) an amine

c. water.

The invention further comprises a single-step process comprising subjecting a nickel-phosphorus alloy containing from 9 to 12% phosphorus deposited on a substrate to a CMP process using a formulation as described above.

In preferred formulations according to the invention the formulation comprises an organic carboxylic acid. This compound attacks the surface and makes removal of the alloy more easily accomplished. Examples of suitable acids include citric acid, oxalic acid, lactic acid, tartaric acid, glycine and mixtures of such acids.

The formulations of the invention are carefully balanced to provide that the attack of the oxidant, (and any organic carboxylic acid present), on the nickel-phosphorus alloy surface is not so vigorous that material is removed in uncontrollable amounts that can not be adequately sequestered by the phosphonate group in the accelerant which is a chelating agent effective to chelate nickel removed from the surface of the nickel-phosphorus alloy and prevent re-deposition, or increase solubility by reacting with ligand providing components in the formulation. An important element of the balance is to maintain the pH at the above level and the level of the second accelerant plays an important role in this regard.

In selecting the oxidant, the most preferred example is hydrogen peroxide because of the purity of the product and because it leaves little or no residue. However other known oxidants, such as periodates, sulphurous acid and percarbamates, can be used in partial or complete substitution for hydrogen peroxide unless there is a

compatibility problem as is the case for mixtures of hydrogen peroxide and potassium periodate. The preferred oxidant is however hydrogen peroxide and most preferably in the form of a 35% by weight solution in water.

The moderator for the activity of the oxidant comprises a phosphite or phosphate group having the group - PO_x, where x is from 1 to 4. The preferred exemplar is phosphoric acid, (including the meta-, ortho-, and pyro-phosphoric acid versions).

The accelerant also comprises chelating phosphonate groups and suitable examples include 1-hydroxyethylidene-1,1-diphosphonic acid (HEDP), aminotri (methylenephosphonic acid) (ATMP), N-(2-hydroxyethyl)-N, N-di (methylenephosphonic acid) (HEMPA) and 2-phosphonobutane-1,2,4-tricarboxylic acid (PBTC).
Of these HEDP is preferred. This component increases the solubility of the nickel removed from the surface and aids in producing a clean surface readily flushed clean of all CMP residues.

The accelerant also comprises amine, amide or ammonium groups and suitable exemplars of such compounds include ammonium hydroxide, ammonium salts such ammonium nitrate, urea, formamide acetate, biuret, ethylene diamine and glycine. Mixtures of such compounds can also be used. This compound also acts as a ligand to keep nickel in a soluble form after removal from the surface.

The amounts of the components in the formulation are preferably as follows:
Abrasive: from 2 to 10 and more preferably from 3 to 6 wt%;
Oxidizer: from 1 to 6 wt% and preferably 1 to 4 wt% of the active oxidant.

Phosphate or Phosphite: from 0.1 to 6 and more preferably from 0.1 to 4 wt%;
Phosphonate: from 0.1 to 6 and more preferably from 0.1 to 4 wt%;
Amine, Amid, Amide or Ammonium from 0.1 to 6 and more preferably from 0.1 to 4 wt%; and
Organic Carboxylic Acid: from 0.1 to 6 and more preferably from 0.1 to 4 wt%.
Water: The balance up to 100wt%

The most preferred abrasive component of the mixture for use on nickel-phosphorus substrates is silica, having a mean particle size of 15 to 120nm, preferably from 15 to 80nm and most preferably from 15 to 60 nanometers. The most suitable silicas have mono-dispersed, essentially spherical particles. Two suitable silica solutions are available as 30% by weight solid dispersions. A-Green Corp. and DuPont AirProducts NanoMaterials manufacture these products under the trade names BESIL-38A and Syton HD-700 respectively. Of these solutions, Syton HD-700 is preferred.

Description of Preferred Embodiments

Examples

A statistically analytical approach was utilized to formulate this invention. In order to eliminate excess variables in the development process, certain equipment and parameters were held constant. These equipment and their parameters were as follows:

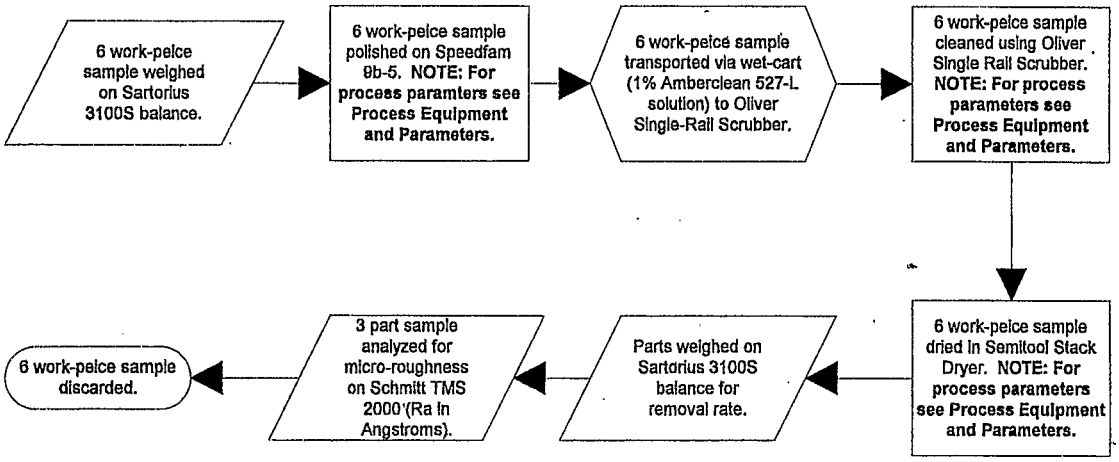
Table A:

• **Polish Machine**	Speedfam 9b-5
— Lower Platen Speed	40rpm
— Sun Gear Radius	3.5 inches
— Sun Gear Speed	9.5rpm
— Ring Gear Speed	8.5rpm
— Carrier Diameter	9 inches
— Number of Work Pieces	6
— Total Down Force	48kg
— Process Time	6 minutes
— Ramp To Down Force	20 seconds
— Total Slurry Flow-Rate	126mL/min
— Polish Pad	Rodel - DPM 1000
• **Roughness Measurement**	Schmitt - TMS
• **Removal Measurement**	Sartorius 3100S Balance
• **Cleaning Machine**	Oliver Singe-Rail
— Double-Spaced	
— Number of Work Pieces	10
— Brush Pressure (air)	40psi
— Soap Time	1sec
— Rinse Time (DI spray)	1sec
— Detergent	AmberClean 527-L
• **Drying Machine**	Semitool Stand-Alone Dryer
— Rotor Speed	2700rpm
— Rinse Cycle	30sec
— DI Flow Rate	.5gpm
— Dry Cycle	180sec
— Air Pressure	60psi

The procedure by which slurry was evaluated through this development process is depicted in the flow chart below:

Table B:

Silica Slurry Evaluation Process Flow Diagram



In addition to holding the procedures and process equipment and parameters constant, the concentration of colloidal silica was held constant at 5.71 percent by weight. This is to say that in every iteration of slurry, the concentration of colloidal silica by weight was held constant at 5.71 percent.

Example 1

This example illustrates the contribution to removal rate by individual chemical groups in the presence of an oxidizer. An initial screening was to be performed involving forty-eight different constituents. At this initial stage of testing, the concentration of hydrogen

peroxide as a thirty-five percent by weight solution was held constant at 2.57. This is to say that during the first phase of the slurry development process hydrogen peroxide in the form of a thirty-five percent by weight solution was held constant in every iteration of slurry at a total percentage by weight of 2.57. Each of the remaining forty-seven constituents was evaluated as a one percent by weight solution comprised of silica as described above, hydrogen peroxide as described above, the specific constituent and the remaining weight percent water. A listing of these constituents and the product codes assigned to them are found in table 1a. The procedure by which each of these constituents was evaluated is according to the Process Flow Diagram depicted in table B. Removal rate data in the form of total grams removal was collected from each slurry evaluated. This data was then analyzed by analysis of variance and a p-value obtained. A p-value of 0.00 was observed indicating that there was greater difference in removal data from slurry to slurry than within the data set acquired for an individual slurry. This is to say that there is sufficient statistical data to make inferences about the performance of each slurry. The data concerning the total removal of the nickel-phosphorous layer facilitated by each slurry is displayed in table 1b.

Table 1a:

Date Run	Code Name	Accelerants	Comments
03/07/01	A0	Hydrogen peroxide, 35%	
	A1	Ammonium nitrate	
	A2	Hydroxylamine nitrate, 50%	
	A3	Monoethanolamine	
03/09/01	A4	Guanidine carbonate	
	A5	Ethylenediamine	
	A6	Aluminum nitrate, 9hydrate	
	A7	Calcium nitrate, 4hydrate	
	A8	Ceric ammonium nitrate	
03/12/01	A9	Chrome III nitrate, 9hydrate	
	A10	Copper II nitrate, 3hydrate	
	A11	Magnesium nitrate, 6hydrate	
	A12	Nickel nitrate, 6hydrate	
03/14/01	A13	Potassium nitrate	
	A14	Potassium stannate, 3hydrate	Incompatibility with hydrogen peroxide, not evaluated
	A15	Zinc II nitrate, 6hydrate	
	A16	Cyanic acid	Possible safety issues existed, not evaluated
03/16/01	A17	HEDP, 60% aqueous	
	A18	Ammonium Fluoroborate	
	A19	Sodium fluorophosphate	
	A20	HPA, 50% aqueous	
	A21	Potassium iodate	
03/19/01	A22	Potassium periodate	Incompatibility with hydrogen peroxide, not evaluated
	A23	Phosphoric acid, 85% aqueous	
	A24	Sodium selenate	
	A25	Ammonium thiocyanate	
	A26	Ammonium vanadate	Possible safety issues existed, not evaluated
03/20/01	A27	Citric acid	
	A28	L-Cysteine	
	A29	Glycine	
	A30	Lactic Acid	
	A31	Oxalic acid	
03/21/01	A32	Tartaric acid	
	A33	Hydrogen peroxide, 35%	
	A34	Urea	
	A35	Oxamide	Possible safety issues existed, not evaluated
	A36	Cyanamide	Possible safety issues existed, not evaluated
03/22/01	A37	Dimethylglyoxime	Incompatibility with hydrogen peroxide, not evaluated
	A38	Manganese II nitrate, 50%	
	A39	Zirconyl nitrate	Incompatibility with hydrogen peroxide, not evaluated
	A40	Tin IV oxide, 15%, 15nm	
03/23/01	A41	Formamid Acetate	
	A42	Formamid Sulfinic Acid	Not evaluated due to unavailability of raw materials
	A43	Mayoquest 1320	
	A44	Mayoquest 2100	
	A45	Taurine	
	A46	Biuret	
	A47	Mayoquest 1200	Not evaluated due to unavailability of raw materials

Table 1b:

Analysis of Variance for Removal

Source	DF	SS	MS	F	P
Slurry A	36	2.827991	0.078555	227.07	0.000
Error	74	0.025600	0.000346		
Total	110	2.853591			

Level	N	Mean	StDev
0	3	0.23667	0.00577
1	3	0.34667	0.01528
2	3	0.40333	0.01155
3	3	0.33333	0.02082
4	3	0.29667	0.01528
5	3	0.41333	0.02309
6	3	0.55333	0.03055
7	3	0.25333	0.03055
8	3	0.36667	0.00577
9	3	0.42000	0.01000
10	3	0.29333	0.01528
11	3	0.06000	0.02646
12	3	0.24333	0.00577
13	3	0.30000	0.02000
15	3	0.21333	0.02309
17	3	0.55000	0.01732
18	3	0.35667	0.00577
19	3	0.46667	0.02887
20	3	0.56333	0.02887
21	3	0.27333	0.00577
23	3	0.56000	0.01000
24	3	0.38333	0.01528
25	3	0.08667	0.00577
27	3	0.58667	0.01528
28	3	0.03000	0.00000
29	3	0.51000	0.01000
30	3	0.54333	0.00577
31	3	0.73333	0.03055
32	3	0.58000	0.01000
34	3	0.27667	0.01155
38	3	0.22000	0.00000
40	3	0.28667	0.00577
41	3	0.50333	0.04619
43	3	0.54000	0.01732
44	3	0.48333	0.02887
45	3	0.25333	0.00577
46	3	0.25667	0.00577

Pooled StDev = 0.01860

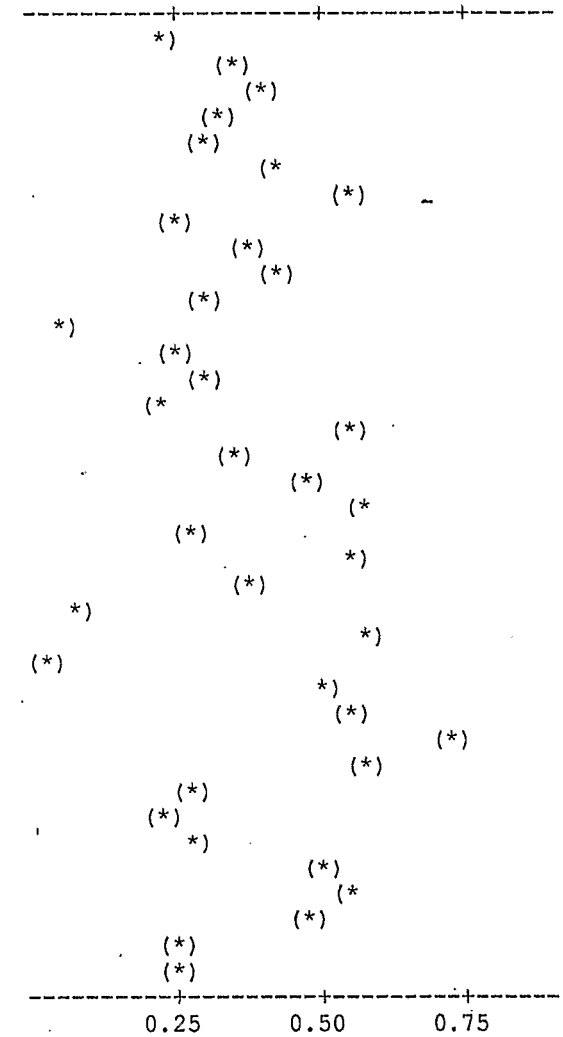


Table 1b, shows a myriad of possible constituents as candidates for slurry with adequate removal rate. Current state of the art colloidal silica slurries remove the nickel-phosphorous layer at rates from 7mg-12mg per minute per disk, which in comparison to this evaluation would equate to .252g-.432g total removal. Table 1b shows

thirteen slurries which surpass this current bench mark and have coded units of A6, A17, A19, A20, A23, A27, A29, A30, A31, A32, A41, A43 and A44. In uncoded units, these constituents are respectively aluminum nitrate, 1-hydroxyethylidene-1,1-diphosphonic acid (HEDP), sodium fluorophosphate, hydroxyphosphono acetate, phosphoric acid, citric acid, glycine, lactic acid, oxalic acid, tartaric acid, formamid acetate, aminotri (methylenephosphonic acid) (ATMP) and 2-phosphonobutane-1,2,4-tricarboxylic acid (PBTC). Each of these constituents in the presence of an oxidizer, (hydrogen peroxide in this specific example) show removal rate capabilities superior to the current state of the art.

Example 2

This example illustrates the effects and interactions of ten specific constituents. A fractional factorial design of experiment model was utilized to approximate the magnitude of interactions of ten constituents up through the third-order. This is to say that through statistical analysis of removal data, the effects individually and interactions with any one or two other constituents were evaluated. Process procedures, parameters and equipment were held constant as described in tables A and B to evaluate constituents with coded units A0, A5, A6, A17, A20, A23, A27, A29, A31 and A32. In uncoded units, these constituents were hydrogen peroxide, ethylene diamine, aluminum nitrate, HEDP, HPA, phosphoric acid, citric acid, glycine, oxalic acid and tartaric acid respectively. A design of experiment model of resolution four was utilized where the forty-two slurries were formulated according to table 2a. Further, this table describes the actual percent

by weight each constituent was present in a given slurry. This is to say that in the first slurry evaluated, denoted by RunOrder 1, constituents A29, A31, A32 and A5 each were present in concentrations of 1 percent by weight of the total solution while A0 was present in 2.57 percent by weight of the total solution. Silica was held constant as described above at a percent by weight of 5.71 and the remaining weight percent was water.

Table 2a:

RunOrder	A6	A17	A20	A23	A27	A29	A31	A32	A5	A0
1	0	0	0	0	0	1	1	1	1	2.57
2	1	0	0	0	0	0	0	0	0	2.57
3	0	1	0	0	0	0	0	0	1	0.00
4	1	1	0	0	0	1	1	1	0	0.00
5	0	0	1	0	0	0	0	1	0	0.00
6	1	0	1	0	0	1	1	0	1	0.00
7	0	1	1	0	0	1	1	0	0	2.57
8	1	1	1	0	0	0	0	1	1	2.57
9	0	0	0	1	0	0	1	0	0	0.00
10	1	0	0	1	0	1	0	1	1	0.00
11	0	1	0	1	0	1	0	1	0	2.57
12	1	1	0	1	0	0	1	0	1	2.57
13	0	0	1	1	0	1	0	0	1	2.57
14	1	0	1	1	0	0	1	1	0	2.57
15	0	1	1	1	0	0	1	1	1	0.00
16	1	1	1	1	0	1	0	0	0	0.00
17	0	0	0	0	1	1	0	0	0	0.00
18	1	0	0	0	1	0	1	1	1	0.00
19	0	1	0	0	1	0	1	1	0	2.57
20	1	1	0	0	1	1	0	0	1	2.57
21	0	0	1	0	1	0	1	0	1	2.57
22	1	0	1	0	1	1	0	1	0	2.57
23	0	1	1	0	1	1	0	1	1	0.00
24	1	1	1	0	1	0	1	0	0	0.00
25	0	0	0	1	1	0	0	1	1	2.57
26	1	0	0	1	1	1	1	0	0	2.57
27	0	1	0	1	1	1	1	0	1	0.00
28	1	1	0	1	1	0	0	1	0	0.00
29	0	0	1	1	1	1	1	1	0	0.00
30	1	0	1	1	1	0	0	0	1	0.00
31	0	1	1	1	1	0	0	0	0	2.57
32	1	1	1	1	1	1	1	1	1	2.57
33	0	1	0	0	0	0	0	0	0	2.57
34	0	0	1	0	0	0	0	0	0	2.57
35	0	0	0	1	0	0	0	0	0	2.57
36	0	0	0	0	1	0	0	0	0	2.57
37	0	0	0	0	0	1	0	0	0	2.57
38	0	0	0	0	0	0	1	0	0	2.57
39	0	0	0	0	0	0	0	1	0	2.57
40	0	0	0	0	0	0	0	0	1	2.57
41	0	0	0	0	0	0	0	0	0	2.57
42	0	1	0	0	0	0	0	0	1	2.57

The quantitative results with respect to estimated effects and coefficients of this evaluation are found in table 2b. The coefficients denoted by "Coef" in table 2b indicate

the magnitude of the effect of an individual constituent or interaction. The statistical significance of these results is described by a p-value which is denoted "P" in table 2b. A p-value less than .05 denotes a statistical significance. This is to say that when a p-value less than .05 is observed, there is sufficient statistical evidence to make inferences about the contribution of an individual constituent or interaction to the system with respect to removal rate.

Table 2b:
Estimated Effects and Coefficients (coded units)

Term	Effect	Coef	SE Coef	T	P
Constant		0.3189	0.002580	123.60	0.000
A6	0.0156	0.0078	0.002580	3.03	0.003
A17	-0.0598	-0.0299	0.002580	-11.59	0.000
A20	0.0348	0.0174	0.002580	6.74	0.000
A23	-0.0127	-0.0064	0.002580	-2.46	0.016
A27	0.0281	0.0141	0.002580	5.45	0.000
A29	-0.0352	-0.0176	0.002580	-6.82	0.000
A31	0.0698	0.0349	0.002580	13.53	0.000
A32	-0.0677	-0.0339	0.002580	-13.12	0.000
A5	-0.0756	-0.0378	0.002580	-14.66	0.000
A0	0.3390	0.1695	0.002580	65.70	0.000
A6*A17	-0.0185	-0.0093	0.002580	-3.59	0.001
A6*A20	-0.0131	-0.0066	0.002580	-2.54	0.013
A6*A23	0.0494	0.0247	0.002580	9.57	0.000
A6*A27	-0.0340	-0.0170	0.002580	-6.58	0.000
A6*A29	-1.0115	-0.5057	0.024878	-20.33	0.000
A6*A31	-0.0140	-0.0070	0.002580	-2.71	0.008
A6*A32	0.0235	0.0118	0.002580	4.56	0.000
A6*A5	0.3246	0.1623	0.010319	15.73	0.000
A6*A0	-0.3925	-0.1962	0.011392	-17.23	0.000
A17*A20	0.0090	0.0045	0.002580	1.74	0.086
A17*A23	-0.0394	-0.0197	0.002580	-7.63	0.000
A17*A27	0.0698	0.0349	0.002580	13.53	0.000
A17*A29	-0.0085	-0.0043	0.002580	-1.66	0.102
A17*A31	0.0131	0.0066	0.002580	2.54	0.013
A17*A32	0.4100	0.2050	0.013772	14.89	0.000
A17*A5	-0.1400	-0.0700	0.007297	-9.59	0.000
A17*A0	-0.3748	-0.1874	0.010319	-18.16	0.000
A20*A23	0.0102	0.0051	0.002580	1.98	0.051
A20*A27	0.4994	0.2497	0.013772	18.13	0.000
A20*A29	1.1023	0.5511	0.025342	21.75	0.000
A20*A31	-0.5858	-0.2929	0.013772	-21.27	0.000
A20*A32	0.1665	0.0832	0.007297	11.41	0.000
A20*A5	-0.4369	-0.2184	0.013651	-16.00	0.000
A23*A27	0.0027	0.0014	0.002580	0.52	0.601
A23*A29	-0.0523	-0.0261	0.002580	-10.14	0.000
A23*A31	0.1598	0.0799	0.007297	10.95	0.000
A23*A32	0.5769	0.2884	0.013892	20.76	0.000
A27*A29	0.1948	0.0974	0.007297	13.35	0.000
A27*A32	-1.0546	-0.5273	0.025210	-20.92	0.000
A29*A32	-0.5333	-0.2667	0.013651	-19.53	0.000
A17*A20*A23	1.0433	0.5217	0.024744	21.08	0.000

Analysis of Variance for Sample1 (coded units)

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Main Effects	10	4.28746	3.29494	0.329494	515.73	0.000
2-Way Interactions	30	0.63145	0.87552	0.029184	45.68	0.000
3-Way Interactions	1	0.28397	0.28397	0.283968	444.47	0.000
Residual Error	84	0.05367	0.05367	0.000639		
Pure Error	84	0.05367	0.05367	0.000639		
Total	125	5.25655				

The beneficial second order interactions obtained from this evaluation are as follows:

Beneficial Interactions

HEDP:Ethylenediamine (slightly significant)
Aluminum Nitrate:Tartaric Acid
Aluminum Nitrate:Glycine
Aluminum Nitrate:Phosphoric Acid
Aluminum Nitrate:Glycine
Phosphoric Acid:HPA (slightly significant)
Citric Acid:HEDP
HPA:Glycine
Aluminum Nitrate:Ethylenediamine (slightly significant)
Citric Acid:Ethylenediamine
HPA:Glycine
Citric Acid:HPA:Glycine
HPA:Ethylenediamine
Phosphoric Acid:Citric Acid
Citric Acid:Glycine (slightly significant)

Example 3

Example 3 illustrates the effects and interactions more specifically of constituents, in coded units, A17, A20, A23, A27 and A29. These constituents in uncoded units are HEDP, HPA, phosphoric acid, citric acid and glycine respectively. Again, process procedures, parameters and equipment were held constant as described in tables A and B. Silica was present in each slurry at a concentration of 5.71 percent by weight of the total solution. Hydrogen peroxide in a 35 percent by weight solution was held constant in each slurry at a level of 2.57 percent by weight of the total solution. A fractional factorial

design of experiment model was created to incorporate these chemistries. By so doing, nineteen slurries were formulated and quantitatively analyzed by examining removal rate data. The design of experiment model is defined in table 3a. A statistical analysis of this data is found in table 3b where the estimated effects and coefficients of individual constituents and interactions up through the forth order are displayed.

Table 3a:

Run Order	A17	A27	A29	A20	A23
1	0.1	0.1	0.1	0.1	0
2	1.1	0.1	0.1	0.1	0
3	0.1	1.1	0.1	0.1	0
4	1.1	1.1	0.1	0.1	0
5	0.1	0.1	1.1	0.1	0
6	1.1	0.1	1.1	0.1	0
7	0.1	1.1	1.1	0.1	0
8	1.1	1.1	1.1	0.1	0
9	0.1	0.1	0.1	1.1	0
10	1.1	0.1	0.1	1.1	0
11	0.1	1.1	0.1	1.1	0
12	1.1	1.1	0.1	1.1	0
13	0.1	0.1	1.1	1.1	0
14	1.1	0.1	1.1	1.1	0
15	0.1	1.1	1.1	1.1	0
16	1.1	1.1	1.1	1.1	0
17	1.0	1.0	0.0	0.0	1
18	1.0	1.0	0.0	0.0	1
19	1.0	1.0	0.0	0.0	1

Table 3b:

Estimated Effects and Coefficients for Sample (coded units)

Term	Effect	Coef	SE Coef	T	p
Constant		0.53518	0.007564	70.76	0.000
A17	0.05403	0.02701	0.002743	9.85	0.000
A27	0.02744	0.01372	0.002743	5.00	0.000
A29	-0.04166	-0.02083	0.003003	-6.94	0.000
A20	-0.04533	-0.02266	0.003003	-7.55	0.000
A23	0.01349	0.00674	0.007677	0.88	0.385
A17*A27	-0.03435	-0.01717	0.002743	-6.26	0.000
A17*A29	-0.02003	-0.01001	0.003003	-3.34	0.002
A17*A20	-0.03286	-0.01643	0.003003	-5.47	0.000
A27*A29	-0.02727	-0.01364	0.003003	-4.54	0.000
A27*A20	-0.03460	-0.01730	0.003003	-5.76	0.000
A29*A20	-0.04084	-0.02042	0.003287	-6.21	0.000
A17*A27*A29	0.03635	0.01817	0.003003	6.05	0.000
A17*A27*A20	0.03451	0.01726	0.003003	5.75	0.000
A17*A29*A20	0.04386	0.02193	0.003287	6.67	0.000
A27*A29*A20	0.03277	0.01639	0.003287	4.99	0.000
A17*A27*A29*A20	-0.00151	-0.00076	0.003287	-0.23	0.819

Analysis of Variance for Sample (coded units)

Source	DF	Seq SS	Adj SS	Adj MS	F	p
Main Effects	5	0.117544	0.100321	0.0200643	56.66	0.000
2-Way Interactions	6	0.049612	0.060841	0.0101402	28.63	0.000
3-Way Interactions	4	0.049292	0.048996	0.0122491	34.59	0.000
4-Way Interactions	1	0.000019	0.000019	0.0000187	0.05	0.819

Table 3a depicts the levels at which each of the constituents were evaluated. For example, in addition to silica and hydrogen peroxide which were afore mentioned, slurry number 3, indicated by RunOrder 3, comprised of .1 percent A17, 1.1 percent A27, .1 percent A29, .1 percent A20 and no A23. Each of the percentages described above are indicative of a percent by weight of the total slurry. The significance of this example is that A29 and A20 are shown to have an adverse effect on removal rate when in the presence of all the other constituents in this specific evaluation. Approximate values of said negative impacts in this specific system are found in table 3b and are characterized by their estimated coefficients, denoted by "Coef".

Example 4

Example 4 depicts the effects of individual constituents and interactions of the preferred constituents in this invention. In coded units, these constituents are A0, A17, A23 and A27. Respectively, these constituents in uncoded units are hydrogen peroxide, HEDP, phosphoric acid and citric acid. All procedures, parameters and equipment were held constant as described in tables A and B. A fractional factorial design of experiment model was utilized to determine the magnitude of contributions with respect to removal rate of each constituent. The fractional factorial design of experiment model is portrayed in table 4a. Silica was present as 5.71 percent by total weight of each slurry. Ammonium hydroxide was utilized to standardize the pH throughout the evaluation at 2.5. Quantitative statistical analysis of the results of this example is available in table 4b. The concentrations of each constituent in each slurry is depicted in table 4a. For example, the first slurry evaluated, denoted by RunOrder 1, comprised of .25 weight percent A17, .25 weight percent A23, .27 weight percent A27 and 1.29 weight percent A0. Said weight percent values are indicative of total weight percent.

Table 4a:

Run Order	A17	A23	A27	A0
1	0.25	0.25	0.25	1.29
2	1.25	0.25	0.25	3.86
3	0.25	1.25	0.25	3.86
4	1.25	1.25	0.25	1.29
5	0.25	0.25	1.25	3.86
6	1.25	0.25	1.25	1.29
7	0.25	1.25	1.25	1.29
8	1.25	1.25	1.25	3.86

Table 4b:

Estimated Effects and Coefficients for Sample (coded units)

Term	Effect	Coef	SE Coef	T	P
Constant		0.59000	0.003773	156.37	0.000
A17	0.04167	0.02083	0.003773	5.52	0.000
A23	0.05000	0.02500	0.003773	6.63	0.000
A27	-0.02167	-0.01083	0.003773	-2.87	0.011
A0	0.03667	0.01833	0.003773	4.86	0.000
A17*A23	-0.03833	-0.01917	0.003773	-5.08	0.000
A17*A27	0.00333	0.00167	0.003773	0.44	0.665
A17*A0	-0.00500	-0.00250	0.003773	-0.66	0.517

Analysis of Variance for Sample (coded units)

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Main Effects	4	0.036300	0.036300	0.0090750	26.56	0.000
2-Way Interactions	3	0.009033	0.009033	0.0030111	8.81	0.001
Residual Error	16	0.005467	0.005467	0.0003417		
Pure Error	16	0.005467	0.005467	0.0003417		
Total	23	0.050800				

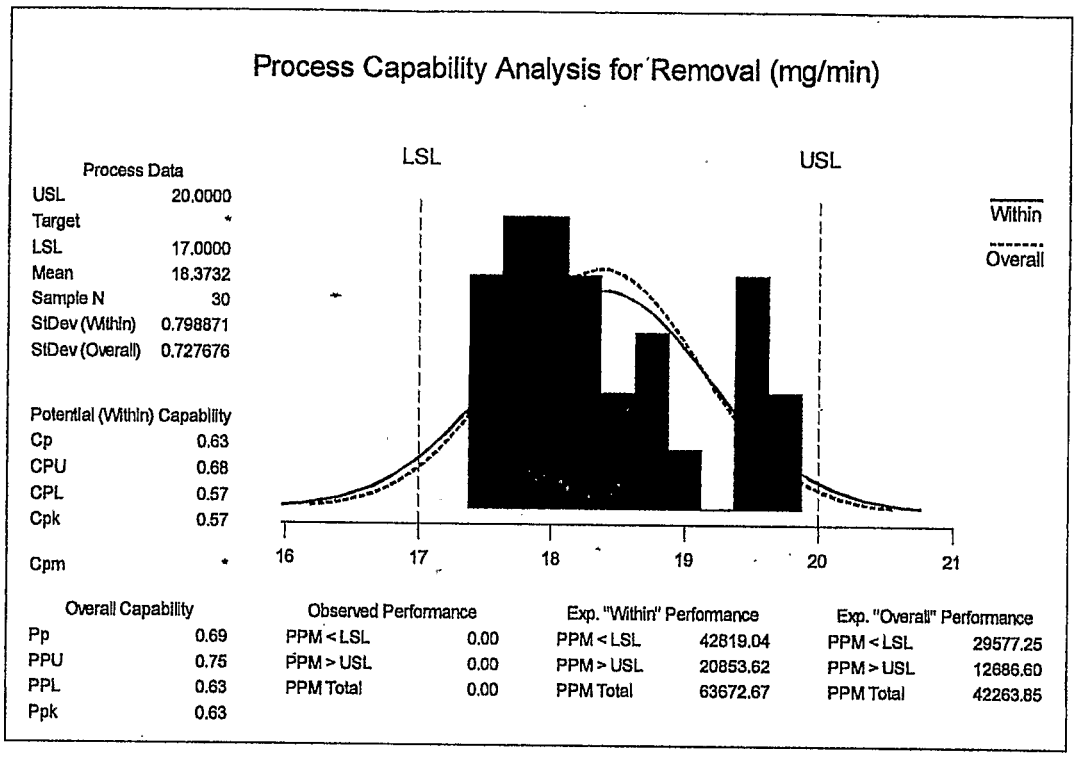
This example illustrates the significant interactions between the preferred constituents in this invention up through the second order.

Example 5

This example illustrates the performance capability of this invention. All process parameters and equipment were held constant as described in tables A and B when slurry comprising hydrogen peroxide, citric acid, HEDP, phosphoric acid, ammonium hydroxide, silica and water was evaluated.

Thirty different runs were performed according to tables A and B. The removal and surface roughness data from these thirty runs were statistically analyzed. Removal rate data is portrayed graphically in table 5a while surface roughness data is portrayed in table 5b. The data acquired from this example depicts a mean removal rate of 18.37mg/min/disk. Accompanying this mean removal rate is a standard deviation of .799mg/min/disk. The surface of the nickel-phosphorous after polishing with this invention is void of defects. Defects are defined as any interruption in the nickel-phosphorous lattice having depth or height greater than twelve angstroms. This is observed through the surface roughness data obtained from this evaluation. A mean surface roughness of 1.47 angstroms was observed with a standard deviation of .17 angstroms. This value of 1.47 angstroms is indicative of the surface condition of the substrate. As measured on a TMS 2000, manufactured by Schmitt Inc., the average difference from peak to valley on the surface of the disks measured was 1.47 angstroms.

Table 5a:



Process Data	
USL	20.0000
Target	*
LSL	17.0000
Mean	18.3732
Sample N	30
StDev (Within)	0.798871
StDev (Overall)	0.727676

Potential (Within) Capability	
Cp	0.63
CPU	0.68
CPL	0.57
Cpk	0.57
Cpm	*

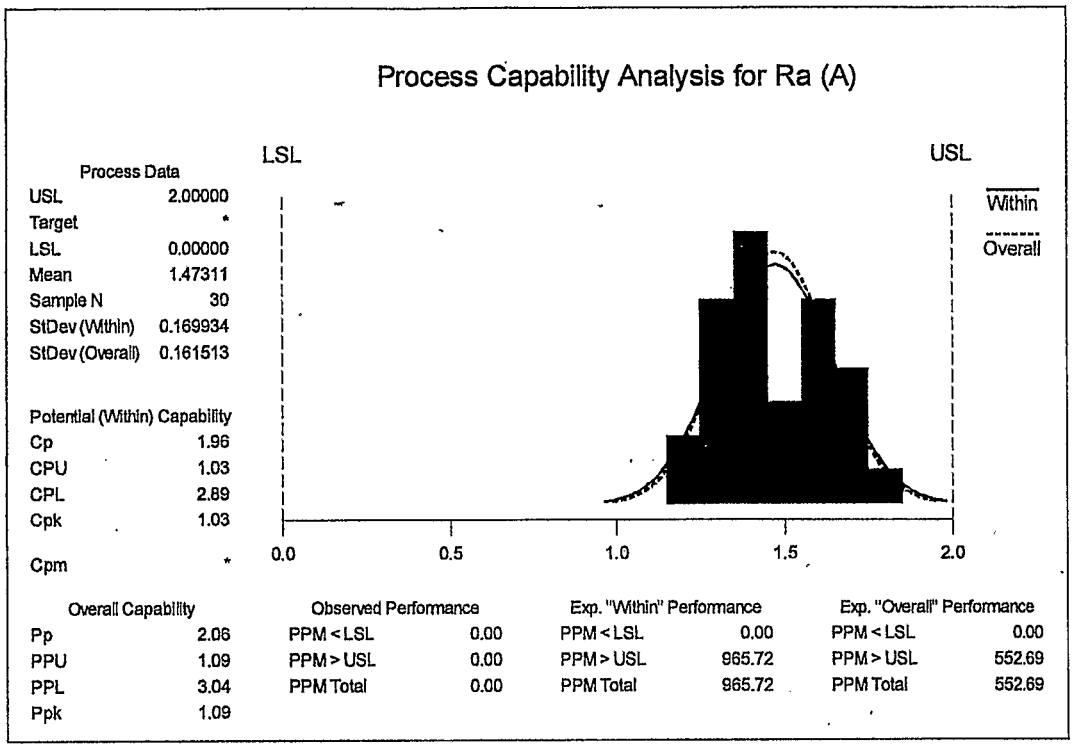
Overall Capability	
Pp	0.69
PPU	0.75
PPL	0.63
Ppk	0.63

Observed Performance	
PPM < LSL	0.00
PPM > USL	0.00
PPM Total	0.00

Exp. "Within" Performance	
PPM < LSL	42819.04
PPM > USL	20853.62
PPM Total	63672.67

Exp. "Overall" Performance	
PPM < LSL	29577.25
PPM > USL	12686.60
PPM Total	42263.85

Table 5b:



Process Data	
USL	2.00000
Target	*
LSL	0.00000
Mean	1.47311
Sample N	30
StDev(Within)	0.169934
StDev(Overall)	0.161513

Potential (Within) Capability	
Cp	1.96
CPU	1.03
CPL	2.89
Cpk	1.03
Cpm	*

Overall Capability	
Pp	2.06
PPU	1.09
PPL	3.04
Ppk	1.09

Observed Performance	
PPM < LSL	0.00
PPM > USL	0.00
PPM Total	0.00

Exp. "Within" Performance	
PPM < LSL	0.00
PPM > USL	965.72
PPM Total	965.72

Exp. "Overall" Performance	
PPM < LSL	0.00
PPM > USL	552.69
PPM Total	552.69

The chemistry utilized to obtain the data depicted in tables 5a and 5b are by what the following claims are made.

We Claim:

1. A CMP formulation which comprises a dispersion of abrasive particles with particle sizes from 15 to 80 nanometers and selected from the group consisting of silica, alumina, titania, ceria, zirconia and mixtures thereof dispersed in a formulation having a pH of from 2.4 to 2.6 comprising:
   a. an oxidant;
   b. a moderator of the action of the oxidizing agent which comprises a phosphate or phosphite group;
   c. a first accelerant comprising phosphonate groups;
   d. a second accelerant comprising amine or ammonium groups; and
   e. water.
2. A formulation according to Claim 1 in which the formulation further comprises an organic carboxylic acid.
3. A formulation according to Claim 2 in which the organic carboxylic acid is selected from the group consisting of citric acid, oxalic acid, lactic acid, tartaric acid, glycine and mixtures of such acids.
4. A formulation according to Claim 3 in which the organic carboxylic acid is present in an amount that is from 2 to 10 wt% of the formulation.
5. A formulation according to Claim 1 in which the abrasive particles are silica particles with an average particle size of 15 to 50 nanometers.
6. A formulation according to Claim 1 in which the amount of abrasive in the formulation is from 2 to 10 wt% of the weight of the formulation.

7. A formulation according to Claim 1 in which the oxidizing agent is selected from the group consisting of peroxides, periodates, percarbamates and mixtures thereof.
8. A formulation according to Claim 7 in which the oxidizing agent is hydrogen peroxide in a concentration of from 0.1 to 6 wt% of the formulation weight.
9. A formulation according to Claim 1 in which the moderator is selected from the group consisting of compounds having the group $-PO_x$, where x is from 1 to 4, and mixtures thereof.
10. A formulation according to Claim 9 in which the moderator is present in the formulation in an amount that represents from 0.1 to 6 wt% of the formulation weight.
11. A formulation according to Claim 1 in which the first accelerant is selected from the group consisting of 1-hydroxyethylidene-1,1-diphosphonic acid (HEDP), aminotri (methylenephosphonic acid) (ATMP), N-(2-hydroxyethyl)-N, N-di (methylenephosphonic acid) (HEMPA), 2-phosphonobutane-1,2,4-tricarboxylic acid (PBTC)and mixtures thereof.
12. A formulation according to Claim 11 in which the first accelerant is present in the formulation in an amount that is from 0.1 to 6 wt% of the formulation weight.
13. A formulation according to Claim 1 in which the second accelerant is selected from the group consisting of ammonium hydroxide, ammonium salts such ammonium nitrate, urea, formamide acetate, biuret, ethylene diamine, glycine and mixtures of such compounds.

14. A formulation according to Claim 13 in which the second accelerant is present in the formulation in an amount that is from 0.1 to 6 wt% of the formulation weight.
15. A process for the chemical-mechanical planarization of the surface of a nickel/phosphorus alloy containing from 9 to 12% of phosphorus which comprises polishing the surface in the presence of a slurry comprising a dispersion of abrasive particles with particle sizes from 15 to 50 nanometers and selected from the group consisting of silica, alumina, titania, ceria, zirconia and mixtures thereof dispersed in a formulation having a pH of from 2.4 to 2.6 comprising:
    a. an oxidant;
    b. a moderator of the action of the oxidizing agent which comprises a phosphate or phosphite group;
    c. a first accelerant comprising phosphonate groups;
    d. a second accelerant comprising amine or ammonium groups; and
    e. water.
16. A process according to Claim 15 in which an organic carboxylic acid is added to the formulation.
17. A process according to Claim 16 in which the organic carboxylic acid is selected from the group consisting of citric acid, oxalic acid, lactic acid, tartaric acid, glycine and mixtures of such acids.
18. A process according to Claim 17 in which the organic carboxylic acid is added to the formulation in an amount that is from 2 to 10 wt% of the formulation.
19. A process according to Claim 18 in which the abrasive particles are silica particles with an average particle size of 15 to 50 nanometers.

20. A process according to Claim 15 in which the amount of abrasive incorporated into the formulation is from 2 to 10 wt% of the weight of the formulation.
21. A process according to Claim 15 in which the oxidizing agent is selected from the group consisting of peroxides, periodates, percarbamates and mixtures thereof.
22. A process according to Claim 21 in which the oxidizing agent is hydrogen peroxide in a concentration of from 0.1 to 6 wt% of the formulation weight.
23. A process according to Claim 15 in which the moderator is selected from the group consisting of compounds having the group $-PO_x$, where x is from 1 to 4, and mixtures thereof.
24. A process according to Claim 23 in which the moderator is present in the formulation in an amount that represents from 0.1 to 6 wt% of the formulation weight.
25. A process according to Claim 15 in which the first accelerant is selected from the group consisting of 1-hydroxyethylidene-1,1-diphosphonic acid (HEDP), aminotri (methylenephosphonic acid) (ATMP), N-(2-hydroxyethyl)-N, N-di (methylenephosphonic acid) (HEMPA), 2-phosphonobutane-1,2,4-tricarboxylic acid (PBTC)and mixtures thereof.
26. A process according to Claim 25 in which the first accelerant is present in the formulation in an amount that is from 0.1 to 6 wt% of the formulation weight.
27. A process according to Claim 15 in which the second accelerant is selected from the group consisting of ammonium hydroxide, ammonium salts such ammonium nitrate, urea, formamide acetate, biuret, ethylene diamine, glycine and mixtures of such compounds.

28. A process according to Claim 27 in which the second accelerant is present in the formulation in an amount that is from 0.1 to 6 wt% of the formulation weight.
29. A process for the chemical-mechanical planarization of the surface of a nickel/phosphorus alloy containing from 9 to 12% of phosphorus which comprises polishing the surface in the presence of a slurry comprising a dispersion of abrasive particles with particle sizes from 15 to 50 nanometers and selected from the group consisting of silica, alumina, titania, ceria, zirconia and mixtures thereof dispersed in a formulation having a pH of from 2.4 to 2.6 comprising:
    f. an oxidant;
    g. a moderator of the action of the oxidizing agent which comprises a phosphate or phosphite group;
    h. a first accelerant comprising phosphonate groups;
    i. a second accelerant comprising amine or ammonium groups; and
    j. water.