COLOR TINTED ELECTROPOLISHED SURFACES: WHAT DO THEY MEAN?

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ABSTRACT
Occasionally, electropolished stainless steel surfaces have shades of gold and blue rather than the normal high gloss colorless finish. These interference colors raise questions because of their perceived adverse effect on WFI or other pharmaceutical products. This paper describes the analyses of the different colored surfaces using XPS (X-Ray Photoelectron Spectroscopy, also known as ESCA, Electron Spectroscopy for Chemical Analysis). The film thickness as a function of color was determined by sputtering and the ratios of the different compounds that make up the film were determined by XPS. The results indicate that some gold color may be better than the colorless film, but the blue layer may be less desirable based on the chemical composition.

INTRODUCTION
Type 316L stainless steel is the material of choice for most pharmaceutical product or water for injection (WFI) systems. The tubing used in these systems normally has the inside diameter (ID) surface finished by either electropolishing or a simple grit polish. Of the two finishes the electropolished surface has the better performance characteristics for these reasons:

1. The chromium to iron ratio is increased from ~0.24:1 to ~2.00:1;
2. The surface roughness is improved from ~20 μ-inches (0.5 μm) Ra to ~5μ-inches (0.13 μm) Ra;
3. The surface is much smoother and does not show the jagged grit lines characteristic of an as-polished surface;
4. The depth of the passive layer, as measured by the depth of oxygen penetration, is significantly increased;
5. Occluded iron contamination, strain transformed martensite and other metallurgical contaminants are removed by the chemical action;
6. Inclusions, especially manganese sulfides, are removed by electropolishing and will not be present to dissolve into the product stream; and
7. Manufacturing defects that may be masked over by the mechanical polishing operation are very visible after electropolishing, including dirt and other contaminants.

A brief explanation of each of these advantages is in order.

The chromium to iron ratio is a measure of the corrosion resistance of the passive layer on all stainless steels. During the passivation process, which can occur in air within several hours after the stainless steel surface has been abraded or otherwise altered, the chromium combines with oxygen and forms an impervious barrier to further reaction of the material below that film. This is an important concept to understand the thesis of this paper. As the chromium content increases the film becomes a better barrier. A ratio of 0.24:1 is the Cr:Fe ratio in the base alloy. During electropolishing the iron and other elements are preferentially dissolved, allowing the chromium to increase in its atomic percentage on the surface. Normally this ratio is determined by Auger electron spectroscopy, producing a chart like that presented in Figure 1. This

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figure shows the variation of the alloying elements as a function of sputtering time. Sputtering is the term used to describe the removal of surface layers of material using highly energized argon ions. This time function is converted into depth from the surface using a standard with a known removal rate. In this case the reference material was tantalum oxide.

After electropolishing the Cr:Fe ratio is increased significantly, up to 2:1. One of the limitations of Auger Spectroscopy is the inability to determine the molecular species within the passive layer under routine analysis conditions. In contrast XPS is a powerful tool because chemical compounds often can be determined by comparison with known standards.

The second advantage of electropolishing is the dramatic improvement in surface finish, not only based upon profilometer readings, but also in actual surface appearance as determined by the scanning electron microscope (SEM). Such an improvement means there are fewer areas of entrapment for product or process contaminants. Electropolished surfaces are easier to clean and trap less debris.

The depth of oxygen penetration, as seen in Figure 1, is a measure of the depth of passive layer. In general, the deeper the oxygen penetration, the more corrosion resistance the material will have. But as we shall later see, this is true only if the oxide species remains as Fe_2O_3, or hematite. If the oxide is present as Fe_3O_4 or magnetite, it may become unstable. Most of the air or oxidizing acid formed passive layers are the hematite variety. The magnetite variety forms when the material is held at higher temperatures. Therefore, there may be a maximum depth of passive layer before magnetite begins to form.

Electropolishing removes occluded iron from the mechanically polished surface. Electropolishing may be though of as electroplating in reverse. In electroplating the work is plated with metal dissolved from the anode and forcibly attached to the work surface. In electropolishing the work becomes the anode and a conductive metal is used as the cathode. Metal is forcibly removed from the work surface (the inside of the tube) by the impressed current, and is driven to the cathode. By careful control of the electrical characteristics, the electropolishing bath chemistry and the process variables, the metals go into solution and do plate the cathode. Oxygen is generated at the tube surface, bathing the dissolving surface in very reactive atomic oxygen, thus leading to the high oxygen concentration on the surface. Hydrogen is generated at the cathode and is swept away by the flowing solution and the moving cathode. Any surface contaminants are dissolved or blasted from the surface. Inclusions in the steel likewise are dissolved or removed from the surface, leaving a "pure" stainless steel surface. This removal of surface metal also removes the smeared metal from the mechanical polishing, making it easier to find surface defects. Mechanical polishing almost always is used as a precursor to electropolishing. About the only time it isn't done is with very small diameter tubing that is produced by drawing through tungsten carbide dies over carbide plugs. This process produces a smooth, highly burnished surface, with surface roughnesses in the range of 10 μ-inches (0.25 μm) Ra.

Occasionally the electropolishing operation will produce a color tinted surface, a light gold, darker gold or even a blue surface. The surfaces are still highly reflective, only they show some color. Locally elevated temperatures cause the phenomenon responsible for the different colors. Electropolishing generates significant heat by ohmic heating of the iron dissolved in the solution and by chemical reactions on the metal surface. As long as the flow of electropolishing solution is maintained at a predetermined rate the surfaces will remain colorless with a high gloss. But if the flow is interrupted for even a brief second, the surfaces become hot and in the presence of the highly reactive oxygen, colors due to oxide film formation will be generated. The lowest temperature oxides are the light gold, then progressing to darker gold and finally to the blue color. If allowed to continue the colors would become glossy gray, then progress to the scaly black.

As a producer of electropolished tubular products we are often asked what these colors mean. This paper presents the first set of results from that investigation. We emphasize that these are first results, and that the program is continuing. One of the main accomplishments of the program is the methodology now in place to evaluate a variety of surfaces. From this program we hope to apply these techniques to determine a better understanding of, and a solution to, the roughing process which plagues so many pharmaceutical plants.

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X-RAY PHOTOELECTRON SPECTROSCOPY

X-ray photoelectron spectroscopy or XPS, is also known as Electron Spectroscopy for Chemical Analysis or ESCA. It is one of the newer analytical tools available to the process industries. In the XPS technique a sample is irradiated with monoenergic soft x-rays and the emitted electrons are analyzed for their energy response.[1] Either Mg Kα x-rays (1253.6 electron volts) or Al Kα (1486.7 eV are normally used. In our study we used monochromatic Al Kα x-rays as the incoming beam. The x-rays interact by the photoelectric effect with the atoms in the surface being bombarded and cause photoelectrons to be emitted. These photoelectrons are generated within about 30Å of the surface, and have a measured kinetic energy (KE) expressed as:

$$KE = h\nu - BE - \phi_s$$

where:

        KE is the kinetic energy
        $h\nu$ is the energy of the photon
        BE is the binding energy of the atomic orbital from which the electron originates
        ϕ_s is the spectrometer work function.

Because each element has a unique set of binding energies, XPS can, in theory, be used to identify and determine the concentration of the elements at the tube surface. Variations in the binding energies can be used to identify the chemical state of the materials being analyzed. In addition to photoelectrons emitted, Auger electrons are also emitted because of relaxation of the excited ions remaining after photoemisson.

In practice, a "survey" scan is initially obtained in the energy range from about 1200-0 eV in binding energy. This is done to determine which elements above atomic number 2 are present. For each element for which binding energy information is required, a narrow window (typically about 20 eV) about the central peak is analyzed in a high energy resolution mode to determine the binding energy of the surface species.

Binding energy values are generally calibrated to an internal standard. Often this is the carbon peak from atmospheric exposure, called adventitious carbon. Dependent somewhat upon the analyst and the instrumentation, the binding energy for adventitious carbon is generally set at 284.7 ± 0.3 eV. In this program, the binding energy was calibrated by shifting the peaks in a linear fashion so the adventitious carbon peak occurred at 284.7 eV.

Peak shifting in XPS can be regarded as a measure of covalency and more ionic compounds, such as intermetallic compounds, may or may not be significantly shifted from the pure metal peak value. The experimental energy determined is then compared to either published literature values of known standards or to theoretical arguments based upon chemical bonding to ascertain the species present. It is not uncommon for published values of desired species to be nonexistent; therefore identification may be less than straightforward. The presence of multiple, overlapping binding energies also makes identification difficult. In this study the literature values were obtained from the *Handbook of Photoelectron Spectroscopy*[1] and from *Practical Surface Analysis by Auger and X-Ray Photoelectron Spectroscopy.*[2]

Quantitative analysis of the data used the sensitivity factors in Briggs & Seah[2] which are based on the calculated yields for pure elements. The concentration information should be taken to be semi-quantitative at best and most properly used for comparisons only.

EXPERIMENTAL RESULTS

The XPS system used for the analyses was a PHI Model 5700. Specimens were analyzed in their as-received state (after an isopropanol rinse) and after 25, 50, 100, 200, 400 and 800 seconds of argon depth profiling, or until the oxide thickness was sputtered completely through. The sputtering rate on the system was 1Å/second, calibrated to a SiO_2 sputtering standard. Therefore, the depth profile provided detailed information of approximately 800 Å of metal surface. It should be noted that

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differential sputtering does occur - not all materials sputter at the same rate. Additionally, sputtering can also cause reduction of oxides.

ELEMENTAL SURFACE ANALYSIS

The results for the surface analysis of the three areas are summarized in Table 1. The data indicate that the oxide layer on the control area was between 50-100 Å, on the gold area between 200-400 Å, and on the blue area between 400-800 Å. This is an important finding since it gives the relative depth of the passive layer. In other words, the passive layer is thicker in areas with color.

Surface carbon is contamination from the alcohol rinse and atmospheric exposure. Carbon quickly decreased to low levels, consistent with clean samples, within 25 seconds of sputtering. Nitrogen, sulfur, and phosphorus most likely are due to the acid used for electropolishing and passivation. The source of sodium and calcium is unknown. Silicon, chromium, iron, nickel, and molybdenum were detected from the base alloy. The elevated silicon is especially interesting since its concentration is greater than the alloy would allow and that it is not a surface contaminant. It has been demonstrated[3] that silicon can begin to segregate to the surface of austenitic stainless steels at temperatures as low as 300-400° C (570 - 750° F). This diffusion is quite rapid at temperatures of 500° C (930° F). No manganese was detected on the surface

Figures 2-5 plot the oxygen, chromium, iron, and silicon concentration respectively as a function of depth. Figure 2 is for oxygen and illustrates the relative oxide depth. The oxide depth in the control area is approximately 100 Å, the gold area approximately 350 Å, and the blue area approximately 700 Å. These depths correspond to an arbitrary oxygen concentration of 10 atomic percent. Figure 3 plots chromium concentration as a function of depth. The control and the gold samples show a high chromium level within the first 100 Å, with a relatively rapid decline thereafter. In contrast, the blue area has a very gradual increase in chromium with a maximum at 200 Å corresponding to a lower maximum chromium concentration than either the gold or control areas. The first 100 Å of the blue area are especially chromium deficient. Figure 4 plots iron as a concentration of depth for the three areas. The iron curves are complementary to the oxygen curves of Figure 2. Figure 5 illustrates silicon as a function of depth. The surface silicon was highest on the blue sample.

BINDING ENERGY INFORMATION

The binding energy of all surface elements detected was analyzed to determine if there was a chemical difference among the three areas. The results are summarized in Table 2. A typical binding energy plot for the control or colorless surface at the 25 Å sputtering depth is presented in Figure 6. This chart illustrates the various peak energy locations and identifies each with the corresponding molecular species. Such plots were determined for each color at each sputtering depth and each peak was correlated to the specific compound from the literature library.

Carbon was similar on all areas analyzed, consisting of adventitious, atmospheric C-C along with C=O as determined from spectra in the literature. The nitrogen on all was primarily nitrogen in an organic matrix, the blue area additionally had some ammonium salt present. Because of the presence of multiple oxides, definitive oxide identification is not possible. The blue and control samples were mixed iron, chromium, and silicon oxides while the gold sample was primarily iron and chromium oxide. The sodium binding energy about 1071 eV is consistent with sodium phosphates or silicates. Somewhat surprising, the silicon on the blue and control were silica as determined from literature spectra, while the gold was a silicate. The phosphorus in all cases was typical of a phosphate. The sulfur was consistent with SO_2 or sulfite. The chromium on the blue and the gold was exclusively Cr_2O_3 while the control area was Cr_2O_3 with a small amount of additional Cr metal. This may imply that the chromium oxide is thicker on the blue and gold samples than on the control sample. Also, the iron was completely oxidized to Fe_2O_3 on the blue and gold, while there was once again a low level of metallic iron on the control sample in addition to the oxide. The chemical state of nickel and molybdenum was unreliable due to low surface concentrations or these elements.

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Table 1
Atomic Percent Concentration of Elements Detected in Control (Colorless), Gold and Blue Areas of Electropolished Tube as a Function of Sputtering Time

Control

Ar+, seconds	C	N	O	Na	Si	P	S	Ca	Cr	Fe	Ni	Mo
0	29.5	3.7	47.5	2.1	2.9	1.9	1.5	0.2	4.0	6.6	0.2	0.0
25	0.9		39.7	0.8	2.7	0.9	0.2	0.2	21.4	29.7	2.9	0.7
50	1.1		22.8		3.6		tr		15.6	50.3	·5.4	1.0
100	0.7		8.9		2.7				11.8	70.0	4.4	1.5

Gold

Ar+, seconds	C	N	O	Na	Si	P	S	Ca	Cr	Fe	Ni	Mo
0	27.3	3.0	48.4	0.7	1.5	2.7	1.0		7.8	7.0	0.3	0.3
25	3.4		51.6	0.7	2.2	3.2	0.6	0.1	19.3	16.3	1.6	1.0
50	1.6		44.3	0.5	1.7	2.2	0.5	0.1	27.0	17.8	3.6	0.6
100	1.3		42.0	0.4	1.4	1.9	0.5		23.3	23.8	4.8	0.6
200	1.1		30.5		0.7	1.1	0.4		21.6	37.5	6.0	1.0
400	0.7		4.3						13.3	74.6	5.5	1.6

Blue

Ar+, seconds	C	N	O	Na	Si	P	S	Ca	Cr	Fe	Ni	Mo
0	25.2	3.0	49.9	0.5	4.2	4.8	0.8		3.5	8.0	0.1	
25	3.5	2.1	53.4	0.7	4.8	5.9	0.2	0.1	10.2	18.5	0.3	0.4
50	2.3	2.0	52.1	0.7	4.4	4.8	0.3	0.2	12.9	18.9	0.9	0.6
100	1.7		50.0	0.4	4.0	4.1	0.5		16.6	20.5	1.4	0.8
200	1.5		44.5	0.5	2.3	3.3	0.5	0.2	20.3	23.6	2.4	0.8
400	1.1		25.8		1.0	1.2	0.1		18.7	47.2	3.9	1.1
800	0.6		2.2		0.8				14.6	76.0	4.0	1.8

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Table 2
Binding Energy in Electron Volts and Chemical State Information at the Surface of the Control (Colorless), Gold and Blue Areas on the Electropolished Surface of Stainless Steel

		C	N	O	Na	Si	P	S	Cr	Fe	Ni	Mo
Control	B.E.	284.7 288.2	399.8 + more	531.3 +more	1071.0	104.0 101	133.1	168.5	576.6 574.5	711.0 707.0	ND	ND
	State	C-C C=O	Org. Mtx.	Cr2O3 Fe2O3 Silica		Silica Silicate	Phos- phate	SO2	Cr2O3 Cr	Fe2O3 Fe		
Gold	B.E.	284.7 288.2	399.6	531.1 +more	1070.9	101.9 102.5	133.1	168.5	576.6	711.0	ND	ND
	State	C-C C=O	Org. Mtx.	Cr2O3 Fe2O3		Silicate	Phos- phate	SO2	Cr2O3	Fe2O3		
Blue	B.E.	284.7 288.2	400.0 401.5	531.2 533	1071.1	104.1	133.1	168.8	576.6	711.0	ND	ND
	State	C-C C=O	Org. Mtx./ Ammon. Salt	Cr2O3 Fe2O3 Silica		Silica	Phos- phate	SO2	Cr2O3	Fe2O3		

DISCUSSION
Data in Tables 1 and 2 and Figures 2, 3, 4 and 5 indicate that the blue surface probably was exposed to significantly higher temperatures than the control sample since the diffusion range of Figures 2-5 is broadened. Chromium and iron oxidation in the blue and gold areas is more complete than on the control surfaces.

Oxide films can grow by two mechanisms. The oxygen (or oxygen ion) can diffuse through the film into the metal, causing the film to grow at the metal-oxide interface. The second possibility is that the metal (or metal ion) can diffuse through the film to the surface and react with oxygen, causing the layer to grow at the oxide-air interface. The iron, chromium, and silicon may have different mechanisms of oxide formation at the electropolishing temperatures to which these tubes were exposed. The shape of the curves in Figure 3 may indicate that at the control and gold temperatures, the same mechanism is operating, while at the blue temperature, a different mechanism is operating.

The important observation is the presence of metallic iron and chromium in the control or non- color tinted surface. This means that both elements are capable of reacting with oxygen from the environment. We do not understand the corrosion mechanisms that occur at these atomic levels. One possibility is that the iron will dissolve into the WFI stream or process solution and manifest itself as red rouge. The other is that the oxygen from the corroding solution simply diffuses into the oxygen rich layer and combines with the iron to form the occluded Fe_2O_3. The first possibility would explain the presence of rouge. But with this comes another question: What is the role of chemical passivation on the presence of the surface elemental iron? Obviously more work must be done to understand the mechanisms.

Because no elemental iron or chromium was found in the gold layer, and because the oxide species for the iron was the same as the non-color tinted sample, the gold color may be preferred from a corrosion viewpoint. Also, the presence of silicates (SiO_3^-) on the gold surface, but the presence of silica (SiO_2) on both the colorless and blue surfaces may indicate that on the gold surface the oxygen is reacting with the silicon because neither iron nor chromium is available. If this is true, then the gold surface may be preferable to the other two on the basis of oxidation potential.

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CONCLUSIONS

The major difference among the three colored surfaces is the variation in oxide thickness: 50-100Å for the non-color tinted surface; 200-400Å for the gold surface; and 400-800Å for the blue surface.

The chemical composition of the blue, gold, and control surfaces is similar with the following exceptions:

1. some metallic iron and chromium was detected on the control samples that was not detected on the blue and gold surfaces,
2. the control and blue samples had silica on their surface while the gold sample had silicates; and
3. the blue surface has a significantly increased silicon concentration and decreased surface chromium concentration.

Conventional corrosion theory would indicate the blue area would be subject to earlier corrosion than the other two surfaces. The long-term operational corrosion effect of this surface is unknown.

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2. D. Briggs and M.P. Seah, Editors, Practical Surface Analysis by Auger and X-Ray Photoelectron Spectroscopy, J. Wiley & Sons, Chichester, 1983.

3. C.L. Briant, "A Study of Surface Segregation in Austenitic Stainless Steels", Surface and Interface Analysis, Vol. 13, pages 209-218 (1988)

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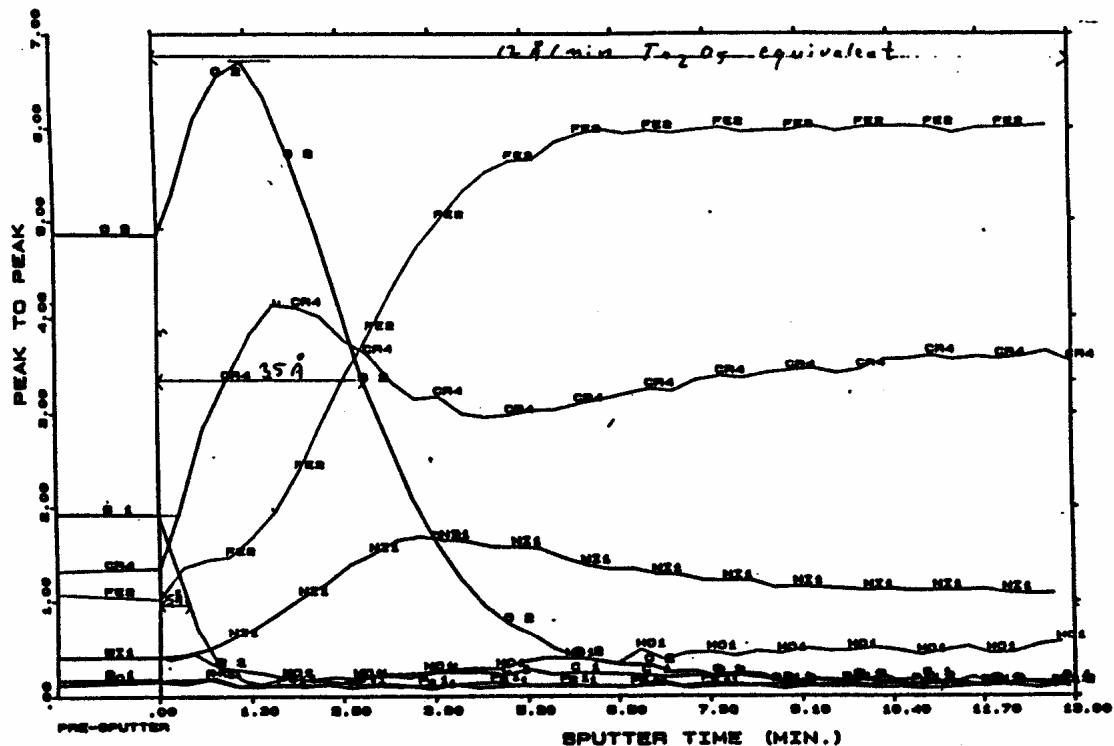
Figure 1. Auger Electron Spectroscopic Scan of an electropolished surface of Type 316L stainless steel showing the change in composition with depth. The composition of the surface is the second line on the left. Composition is in atomic percent.
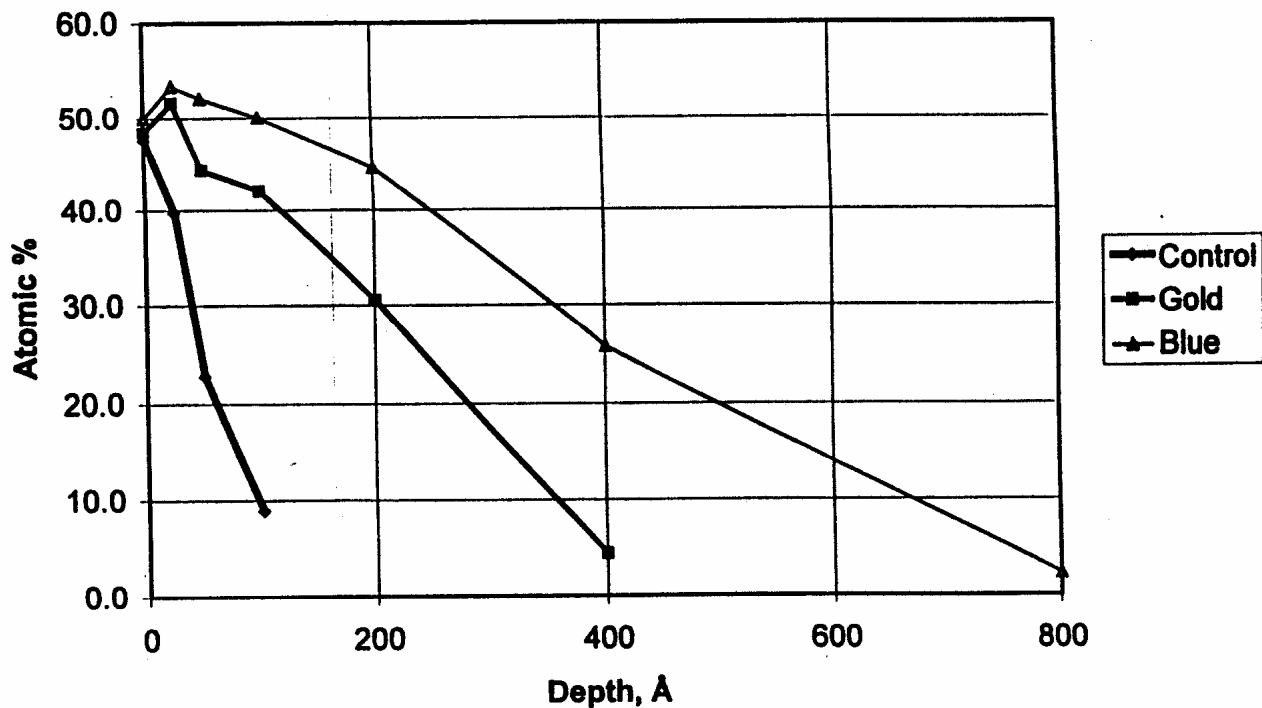
Figure 2: Oxygen Concentration an a Function of Depth from the Surface.
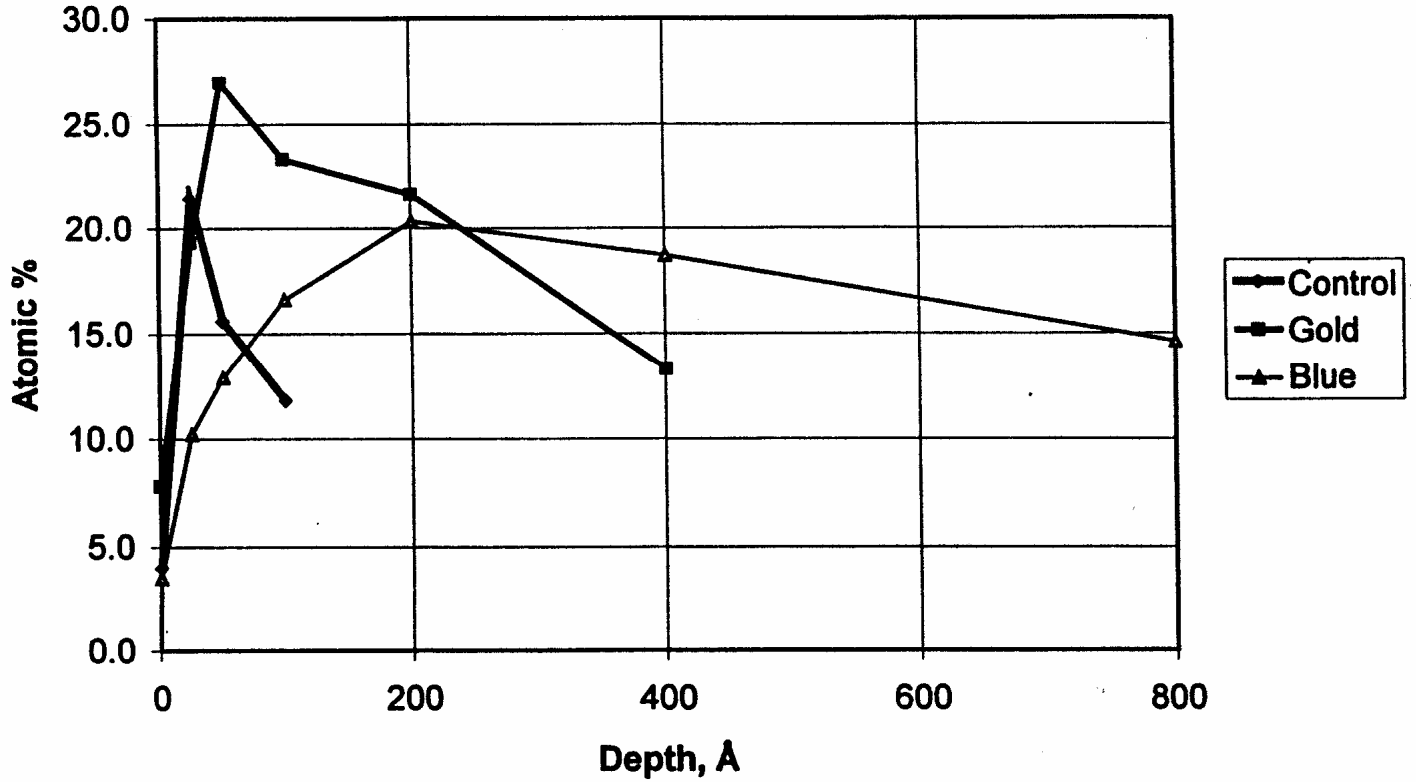
Figure 3:   Chromium Concentration as a Function of Depth from the Surface.
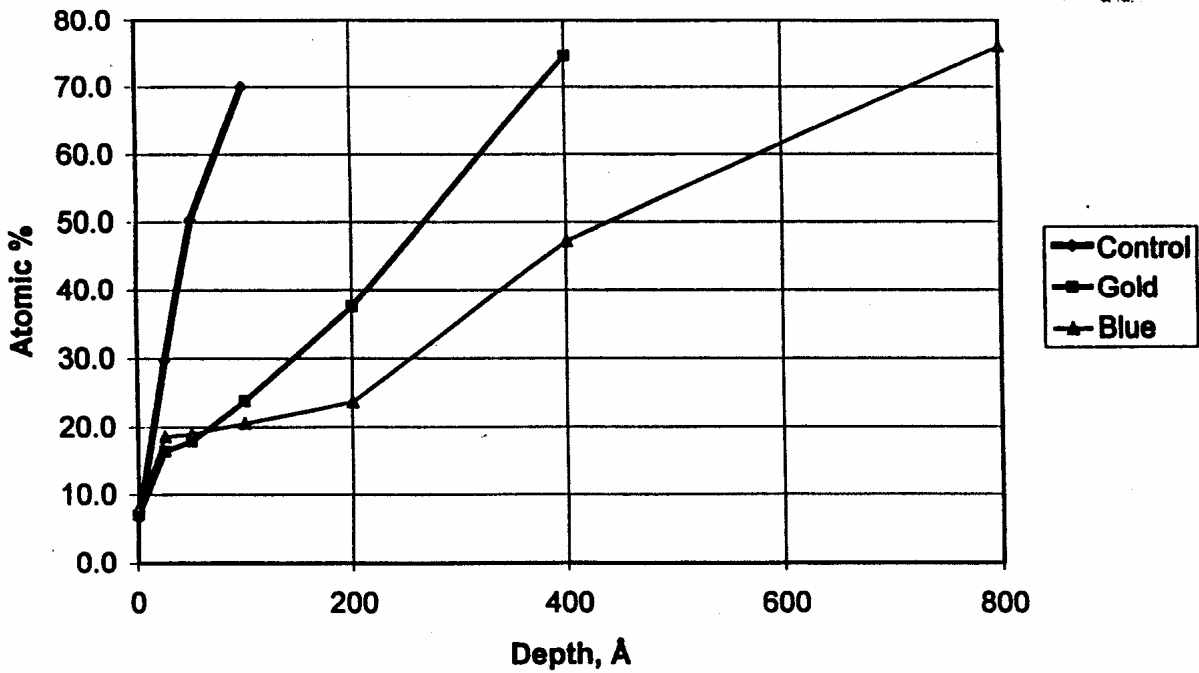
Figure 4:   Iron Concentration as a Function of Depth from the Surface.
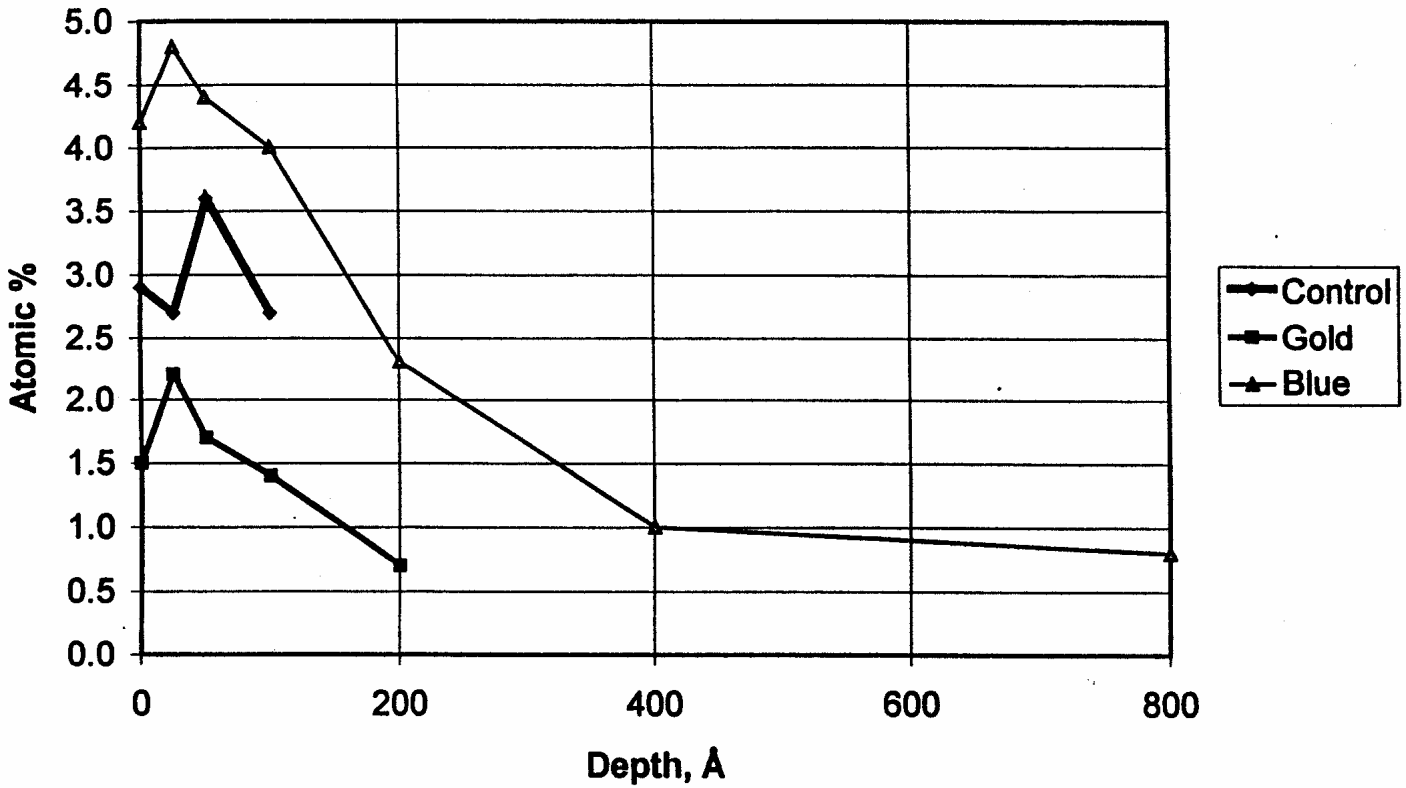
Figure 5.   Silicon Concentration as Depth from the Surface.
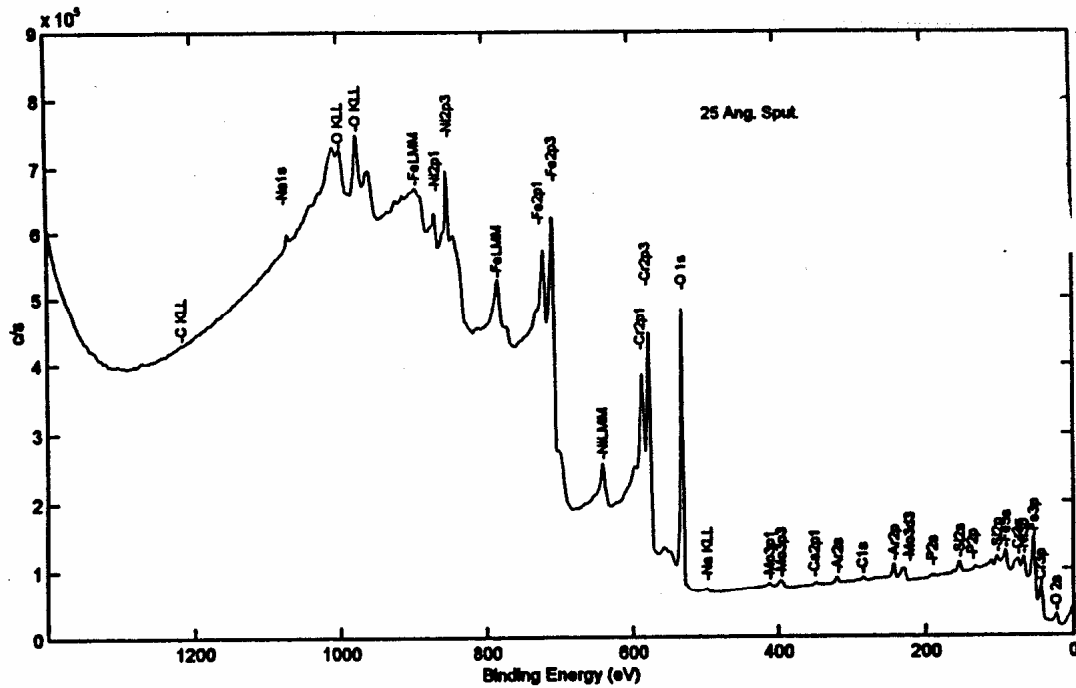
Figure 6:   Typical Binding Energy Spectra at 25Å Sputter Depth for Clear (Colorless) Surface.

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