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Cleaning Procedures in Preparation for Coating

The Need for Clean Surfaces

We have discussed in CERAC Coating Materials News the procedures and processes for preparing materials for deposition, and various deposition techniques. A important procedure for achieving high quality optical coatings is the cleaning of the surface. Surfaces of glass and polymers that are to be coated must be properly cleaned and prepared to insure strong adhesion bonds and high optical quality coatings. The goal is mechanically durable films with no scatter that might result from stress crazing or residual particulates. We have discussed in CMN the importance of chemical and physic-chemical conditioning of surfaces to promote nucleation and the growth of dense coatings. Surfaces that are to be coated must be free of contamination in the form of condensed volatile materials, for example hydrocarbons and organic materials, to the level less than one monolayer (~1 nm), and free of residuals from the polishing process. Cleaning methods have been outlined previously, and in this issue we go into greater detail concerning surface cleaning processes, agents, and testing that precede deposition of coatings.

To produce optical coatings, surfaces must be free of adherent particles and be chemically receptive to the condensing and nucleating adatoms. In the most critical applications involving high energy laser radiation, sub-microscopic particulates and invisible contaminant layers will lower the damage threshold. Variations in cleaning agents and procedures have been developed for different glass and polymer compositions. They have been designed to preclude damage to the surface or the creation of reaction products, either of which can interfere with chemical bonding [1, 2].

Glass Types

Glass compositions range from the common to exotic optical lens glasses. Sodalime glass used in windows and microscope slides is the most common composition and contains 13% sodium oxide. Sodium ions can be leached from the surface during cleaning chemistry, leaving a modified surface. For example, immersion in deionized water will remove alkali metal ions such as sodium. The modified surface can then convert to sodium hydroxide in humid air. Reaction with carbon dioxide can also occur to leave a white layer of sodium carbonate. These altered surface layers must be removed to insure adhesion. Often dissolving them in water followed by drying and storage in a dry atmosphere is adequate preparation for coating. Float glass is produced by cooling the molten glass over a surface of molten tin which gives it a molecularly smooth finish. However, ions of tin diffuse into the surface making that surface unsuitable for optical coating. That surface fluoresces under UV illumination.

Borosilicate glass (trade name Pyrex) has the composition of 96% silica with the remainder mostly boron oxide. Aluminoborosilicate glass is a glass of higher optical quality since it has a lower density of straie and other internal inhomogeneities. Corning 1737F glass was until recently widely used for electro-optical panels in the display industry because it exhibited durable and high-quality optical coating properties. It has been replaced with C Eagle 2000 XG. Pure silica in the form of fused silica, sometimes called fused quartz, is more stable chemically than glass compositions, and therefore can be cleaned by stronger acidic solutions without surface damage. High-quality optical glass of index (d) 1.52 is borosilicate crown known as BK-7. Specific cleaning procedures have been developed for these glass types.

Polymers used in the optical industry for display panels, ophthalmic lenses, and protective / display visors are typically constructed of the following polymer compositions: PMMA (acrylic), polystyrene, poly-carbonate, or Ultem 1010 (PEI). Each has its own mechanical and optical properties, but all are softer than glass and require coating to increase scratch resistance. CMN issues discussed the cleaning and activation of

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polymer surfaces for nucleation and adhesion promotion using neutral or reactive gas ions and electrons in a plasma or by UV/ozone exposure [3].

Cleaning metals mainly consists of the removal of oxide layers, often with acidic etchants. This is especially important for semiconductors where an insulating layer of uncontrolled thickness and composition that grows by spontaneous oxidation is not desired. For reactive metals such as mirror substrates made of aluminum or beryllium and coatings of silver or aluminum, a barrier layer is deposited on the mirror blank to prevent inter-diffusion and degradation of reflection properties. This might be plated nickel or vacuum deposited chromium or a dielectric.

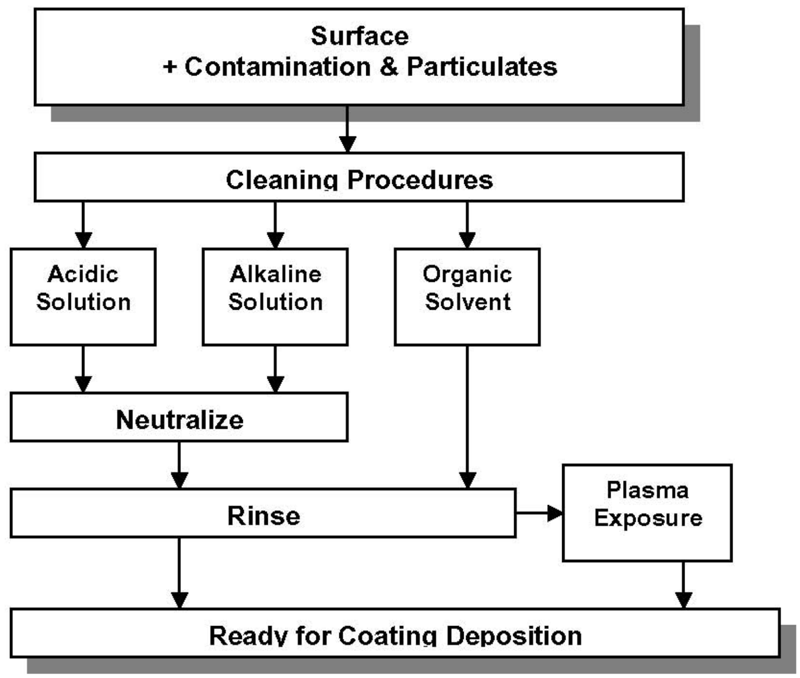

Figure 1: Cleaning Procedure for Optical Coating

Cleaning Procedures

Procedures used in production coating fall into two categories: wet chemical involving solvents, and dry involving plasma of energetic ions and electrons. Figure 1 outlines the primary cleaning procedures and the typical cleaning sequence. The steps can be mixed, for example it might be necessary to clean a surface with both organic and aqueous solvents. Gross removal of contaminants is done before the final step of plasma cleaning. Testing for the state of cleanliness often re-contaminates the surface and it must be re-cleaned.

Solvent Cleaning

Solvents, both organic and aqueous, are used for glass surfaces. For production of large volumes of coated glass, an ultrasonic cleaner and drier is used. The aqueous solution contains a detergent and surfactant. Ultrasonic cleaning is effective in removing large particles, but removal of micro-meter sized particulates requires greater mechanical energy such as provided by a high velocity water jet. The response to cleaning procedures differs between mechanically polished optical components, and fire polished or float polished surfaces. Mechanical polishing creates micro-scopic defects and surface damage that behave differently to the cleaning chemistry. Defects might be enlarged and surface damage either removed or increased. The procedure used must be modified for optical glasses of different chemical durability.

An acidic cleaning solution will not etch glass or silica, but can leach components from the surface. Outside of the ultrasonic baths, an acidic cleaner consisting of 2 parts conc. sulfuric acid and 1 part hydrogen peroxide provides a strong oxidizing agent for stubborn organic contamination [1]. Cleaning occurs at 90° C for 2 min. This must be done under a fume hood for safety. Alkaline cleaning solutions based on sodium or potassium hydroxides in either water or alcohol will lightly etch a glass surface. Immersion should be restricted to a few minutes. If the pH is >9, strong etching will occur. A favorite commercial alkaline surfactant is Alconox. Following alkaline or acid cleaning, the surface should be neutralized or passivated and then flushed with pure water.

Acids and surfactants will not remove silicones, organic solvents such as acetone and alcohol must be used. HF at a concentration of a few percent in water can remove siloxanes, but there is the danger of etching that produces surface roughness and optical scatter.

Tests for "Clean"

Surfaces should be coated as soon after cleaning as possible. Exposure to air of the high-energy surface that cleaning produces invites contamination and particulate collection. What tests tell us whether our surface is clean? A surface is judged "clean" when water uniformly wets it. A continuous sheet of water should adhere to the surface when it is held nearly vertical. Spotting or breakup of the water film signals incomplete cleaning. A more quantitative technique is to measure the contact angle of a drop of deionized water on the surface because this is a measure of surface energy or surface tension. An angle larger than ~20° is suggestive of an hydrophobic condition and characterizes a surface that retains contamination of some kind. A clean surface will produce a contact angle approaching 5° [2]. Care must be exercised to thoroughly remove all traces of surfactant and detergent by rinsing to avoid false indication. Another qualitative technique is exhaling onto the surface. If a uniform fog nucleates, the surface is (or was) c leaned. But re-cleaning is now necessary. A clean surface has a high coefficient of friction, and this can be felt or detected by contact with a metal point. The final rinse is blown off the surface in a way that avoids streaking. Residual invisible water paths or contamination is often made visible by the applied coating, much to the coating operator's dismay.

Dry Cleaning

A final cleaning step that is effective in removing contaminant hydrocarbons and other organic materials that can condense on a surface after wet cleaning is to expose the surface to an energetic plasma immediately before coating deposition. This non-contact process is required to avoid scratching during abrasive wet cleaning and to condition for the different chemistry of polymer surfaces. It is done in the coating chamber at moderate pressures.

Oxygen plasmas create an acidic, while nitrogen produces an alkaline chemistry [2]. Oxygen plasmas are very effective in oxidizing residual hydrocarbon and other organic contamination. Argon plasmas are useful in decomposing and desorbing organics. Mixtures of gases are typically employed in practice, according to the polymer type [3]. UV energy can break bonds and set up increase reaction energy, and is another cleaning mechanism. Activation in a coronal or RF-generated discharge creates chemical radicals and functional groups that readily form strong bonds with the deposited coating material. These cleaning processes are well known in the ophthalmic coating industry. It is important to know that the surface modification generated is not stable, and over time the surface energy will return to a lower state, thus reducing the reactivity and potential for strong adhesive properties. Therefore coating must occur soon after conditioning. In the case of plasma cleaning within the coating chamber, coating deposition should follow within minutes.

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