Novel Substrates for Preparing Free Films from Paints or Polymers

In determinations of mechanical and swelling properties of paints or polymers it is most desirable to be able to work with free films completely detached from their substrates. Various methods of obtaining free films have been used by different investigators. Films have been applied to tinfoil,[1-5] silver-coated glass,[6] or tin-coated steel[7-9] and freed by removing the tin or silver as a mercury amalgam. Free films have also been achieved by drawing coatings on gummed paper,[9] photographic print paper,[10,11] paper coated with hydrolyzed poly(vinyl acetate)[12] or glass coated with methyl cellulose;[13] later the films are soaked loose with water. Other investigators have made free films by stripping them from polyethylene[5,14] or Teflon[15] substrates.

A number of the methods listed have been tried in this laboratory, but each presented difficulties in making free films. Mercury is toxic, easy to spill, and hard to clean up. Films made with mercury frequently have small droplets of amalgam clinging to them, which are not easily removed. Tinfoil can be smoothed and fastened in place over a flat surface, but if large-sized films are required, tinfoil wrinkles while films are being drawn. Some wrinkling also invariably occurs when a relatively large sheet of foil and its coating are removed from the flat backing. Methods that involve water soaking cannot be used with polymers or paints that react in some way with water.[15]

The relatively low surface energies of Teflon and polyethylene usually allow dried films to be stripped without difficulty, but it is not always simple to obtain specular surfaces on Teflon. Slight variations in thickness within a sheet make it hard to get films of uniform thickness when coatings are applied with a drawdown bar or doctor blade. Moreover, the required smooth, flat surfaces of both Teflon and polyethylene are easily damaged in use.

In our laboratory, to avoid some of the problems encountered with Teflon or polyethylene substrates, we have used glass surfaces on which a suitable material has been chemisorbed. These treated glass surfaces are dimensionally stable and remain smooth unless scratched.

Treatments must be applied to clean surfaces. Glass plates or sheets 10 × 12 in. or smaller are cleaned in dichromate–sulfuric acid, thoroughly rinsed, and then dried. To get a fluorocarbon-like coating on the surface, the cleaned glass is swabbed with a liquid solution of a fluorochemical–silicone compound, which reacts with siliceous surfaces. Examples of such chemicals are Minnesota Mining and Manufacturing Company's L-1653 or L-1668 solutions, marketed as mold or adhesive-release agents. After application the compound reacts with glass, causing an orientation that results in a fluorine-containing surface that has a very low critical surface tension of wetting.

To produce hydrocarbon surfaces, clean glass sheets or plates are dipped into a solution containing 0.8 mmoles of an alkyl quaternary ammonium salt in 1 liter of water. Such compounds are frequently used as cationic surface-active agents. Although similar materials would undoubtedly serve as well, we treated out glass with a dialkyl quaternary ammonium chloride having, according to the manufacturer's specifications, alkyl groups of 16 carbons or more. This material chemisorbs onto glass surfaces from aqueous solution[16] and forms a surface composed of hydrocarbon groups when the glass is withdrawn from solution.

The treated glass surfaces are not wet from water; however, they may be cleaned, without damage to the coating, with soap and water, mineral spirits, *n*-hexane, 1,1,2-trichloroethane, or any of a number of other organic solvents. A fluorochemical surface is not harmed by dichromate–sulfuric acid and, consequently, may be cleaned with this reagent, but dichromate cleaning solution removes a hydrocarbon surface completely and cleans the glass sufficiently so that it must be retreated.

The number of films that can be drawn on each treated glass depends on the quality of the initial surface treatment. Fluorochemical surfaces have been reused more than twelve times without requiring intervening treatment other than cleaning. Although they do not appear as durable as the fluorochemical ones, surfaces composed of a chemisorbed layer of quaternary ammonium salt on glass have also been reused a number of times without additional treatment other than cleaning.

As with Teflon and polyethylene, difficulty is occasionally encountered because some paints and polymer solutions will dewet and retract after application to fluorochemical or hydrocarbon surfaces. This problem is usually overcome by placing cellulose tape around the edges of the plates. Coating material wets and clings to the tape, and any tendency to dewet and retract is overcome.

Our films are applied with either a doctor blade or a drawdown bar. Films are easily removed while in a rubbery state. Films too weak at room temperature can often be peeled from substrates at a lower temperature. Films come off fluorochemical surfaces better than from hydrocarbon ones. On both types of treated glass surface we have prepared free films from linseed oil, poly(acrylic acid), poly(vinyl alcohol), poly(vinyl chloride), and a trisamino oil from linseed fatty acids.

Mention of firm names or trade products does not constitute endorsement by the U.S. Department of Agriculture.

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