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SUPERHARD TRANSPARENT COATINGS

MARKS POLARIZED CORPORATION

PREPARED FOR
ARMY AIR MOBILITY RESEARCH AND DEVELOPMENT
LABORATORY

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SUPERHARD TRANSPARENT COATINGS

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153-16 10th Avenue
Whitestone, N.Y. 11357

April 1975

Final Report

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The purpose of this work is to develop and provide a superhard coating (Moh hardness > 5) which is transparent and which will adhere to various polymeric sheet substrates. This coating is to protect helicopter transparencies from scratching and objectionable visual effects, and to avoid frequent replacement. These coatings comprise submicron hard particles in a polymeric matrix. Submicron particles of various compositions and shapes were incorporated in a compatible solution of a polymeric matrix

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coated on a substrate and tested to determine their physical and optical properties.

It was confirmed that the submicron particles in such coatings produce optically clear superhard compositions. The compositions selected comprised a dehydrated polyvinyl silicate chemically bound to silica or aluminum oxide particles. Needle particles were found to produce results superior to spherical or amorphous particle shapes. Shrinkage of the coatings during dehydration is preferably accompanied by corresponding shrinkage of the substrate. Optimum compositions were determined in the system silica/polyvinyl alcohol/aluminum oxide. One of the optimum compositions, silica/polyvinyl alcohol 70/30, contained submicron silica crystallites having a diameter of about 20 Å.

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INTRODUCTION

This concept envisions a transparent plastic material which is superhard because it employs a transparent polymer or coating containing hard submicron particles in suspension. The submicron particles do not appreciably scatter light because their diameter is less than about 2% of a wavelength of visible light at 5500 Å; that is, about 100 Å.

DEFINITION

The term "superhard material" designates a material having a hardness or abrasion resistance of at least 5 on the Moh Scale.[1]

The hardest plastic known, polyallylglycol carbonate, has a hardness of about 3.2. Glass has a Moh hardness of about 6; diamond, 15.

TECHNICAL OBJECTIVE

To produce a superhard transparent composite polymer, or a coating for a polymer, which has:

1. Hardness or abrasion resistance of at least 5 on the Moh Scale; preferably more.
2. Flexibility, impact resistance, and weathering to meet existing specifications for helicopter transparencies.

BACKGROUND

This corporation has done R&D work on hard coatings for many years. Our objective was to provide an abrasion-resistant coating for ophthalmic lenses, automobile windows and the like. As a result of the early work, we obtained a patent on an abrasion-resistant coating. Our work with many polymers convinced us that a new approach was needed. Our work in the apparently unrelated field of electro-optic dipole fluids and devices resulted in a publication,[2] patent, and products which provide know-how on the production and properties of submicron particles. We found that transparency is achieved with suspensions of submicron particles having a diameter of 100 Å or less. Certain submicron particles are hard: quartz, 7; aluminum oxide, 12; silicon carbide, 13; and diamond dust, 15.

This work led us to a new concept of a superhard transparent composite polymer on which we obtained U. S. patent No. 3,751,326, in which the mathematical physics theory of superhard transparent materials, formulations, production techniques and predicted properties are set forth.

The R&D work leading to U. S. patent numbers 2,432,113; 3,324,055; 3,751,326; and 3,846,161; covered a period of about 32 years and utilized about 20 man-years of work. The present contract utilized about 3 man-years of work. The polyvinyl-silicate compositions described in patent No. 3,324,055 include a cross-linking monomer. The compositions described herein are covered by one or more of these issued U. S. patents.

Our work in large-area optically clear coating was started about 1948. We have U. S. patent No. 2,632,725, dated March 24, 1953, entitled "Method of Laminating Lenses" on the spin coating and U. S. patent No. 2,721,809, dated October 25, 1955, entitled "Method for the Uniform Coating of Large Surfaces" on the flow coating.

In the R&D work prior to the filing of patent No. 3,324,055 in 1963, experiments with silicate/polyvinyl alcohol copolymers produced films which were water-absorbant. Subsequently, to overcome the water-absorbancy, work was done with polyvinyl copolymers and with cross-linking monomers not soluble in water when reacted. Cross-links occurred between hydroxyls on polyvinyl chains, polysiloxane chains and the monomer. A typical temperature/time used to cure the coating was 55°C for 1 hour, 68°C for 4 hours, and then 100°C for ½ hour, or 120° to 140°C for 2 minutes.

Composition 129c employs fully hydrolyzed polyvinyl alcohol with substantially no acetate copolymer groups, and no added monomer. Cross-linking occurs only between adjacent polyvinyl and siloxane chains. Partial cross-linking of 129c produces highly cross-linked polyvinyl silicate crystallites embedded in an amorphous polymeric matrix having unreacted hydroxyls. At this stage, the water-permeability of the coating is due to unreacted hydroxyl groups which are hydrophilic. By increasing the heating time to greater than 6 hours at 80° to 100°C, the remaining hydroxyl groups are reacted and cross-linked and the composition becomes compact, hard, craze-resistant, and water-impermeable.

Present helicopter transparencies usually comprise stretched acrylic plastics, which are readily scratched, producing objectionable visual effects and thus requiring frequent replacement at substantial cost. The present work produced a superhard composition which may overcome the need for replacements and thus decrease the time and expense involved. The composition should withstand airloads, provide good optical qualities for vision, be resistant to shattering, and be relatively invulnerable to scratching. All compositions hereinafter described are given in parts by weight.

DISCUSSION

PHYSICAL CHEMISTRY OF SUBMICRON PARTICLE/POLYMER COMPOSITES

Small crystal needles of silica have sometimes been observed in concentrated water/alcohol solutions of polysilicic acid.

The hardness of the silica/pva films may be due to the formation of silica crystallites suspended in an amorphous silica/pva phase.[3] These silica crystallites may have the hardness of quartz. Quartz is crystallized silica, which has a Moh hardness of 7.

Similar crystallite-amorphous regions are known to occur in other polymers such cellulose.[4]

Figure 1 shows an X-ray picture of a silica/pva coating 70/30 (No. 129c), having a thickness of approximately 4 microns. The coating was removed from a nonadherent substrate before X-ray analysis. The X-ray analysis is interpreted as showing submicron silica crystallites of the order of 20 to 40 Å in diameter with a halo at 3.8 Å. The SiO spacing characteristic of quartz is 1.6 Å.[5]

The hard coatings obtained with hydrophilic particles are attributed to their strong chemical bonding. The soft coatings obtained with hydrophobic particles are evidently due to the absence of chemical bonding.

Hydrophilic particles such as alumina and silica in water are surrounded by hydroxyl groups (OH). The hydroxyl groups are known to be capable of reacting with other reactive groups on polymers or particles. For example, polyvinyl alcohol has OH groups and polymethacrylic acid has carboxyl COOH groups. These form a clear suspension with the submicron hydrophilic particles.

The hydroxyl groups on the matrix composition and the hydroxyl groups on the component react, forming strong bonds: Al-O-Si, Al-O-C and Si-O-C. These cross-links strongly bind the particles to the matrix, forming a hard, transparent coating. Water is a reaction product which is eliminated. This is termed a dehydration reaction.

From these considerations and Figure 2, these principles are inferred: (1) to produce a superhard coating, the matrix must chemically bond the hard particles; (2) suspending the submicron particle in a matrix having

Figure 1. X-ray Photo of Silica/pva (70/30) Coating.

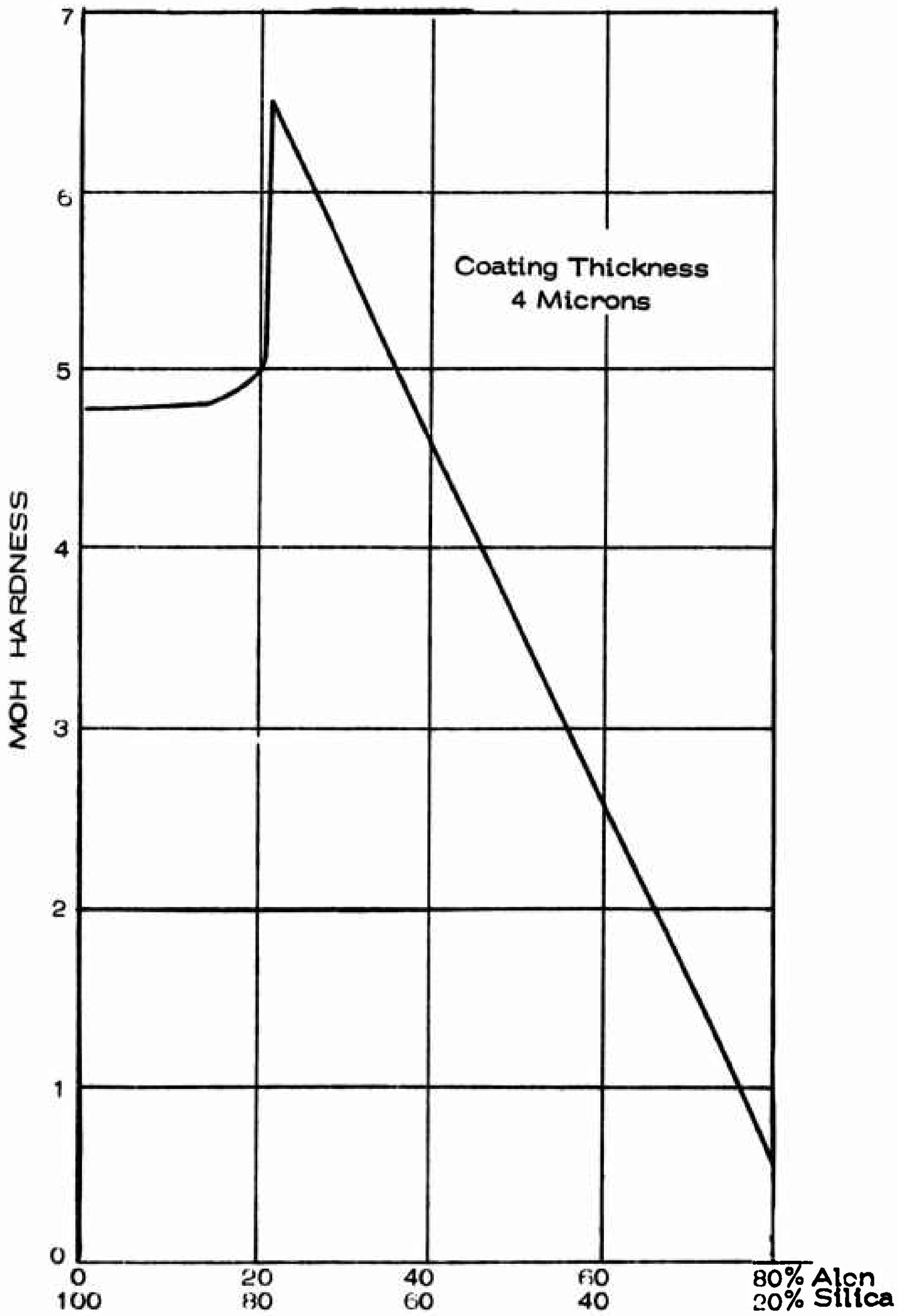


Figure 2. Moh Hardness vs. % Silica/% Alon on Glass.

a greater bonding power will increase the hardness; (3) the hard particles must be present in sufficient proportion; (4) too great a proportion of hard particles and too small a proportion of binder produce a weak structure, from which particles are readily torn away and the structure is soft; (5) for peak hardness there is a composition having an optimum proportion of particle/binder.

FILM TRANSPARENCY VS. PARTICLE DISPERSION IN MONOMERS AND POLYMERS

Case I is diagrammatically shown in Figure 3. The figure shows submicron particles (1) as particle aggregates (2). The aggregates are present because the suspension is not fully dispersed. Fluid molecules (3) are shown by small circles. The fluids may comprise monomer molecules small enough to penetrate the interstices of the aggregates. However, a polymer or chain-like molecule such as (4) is too large and surrounds, but does not penetrate, the aggregate.

If the aggregate (2) is mixed into a fluid containing polymer molecules, the fluid suspension is clear; but upon drying, the film becomes milky, or scatters light.

Case II is diagrammatically shown in Figure 4. In this figure, separated submicron particles (1) are dispersed in a solvent (3) and mixed with a compatible polymer (4). The polymer molecules are contiguous to and separate each of the particles. As a result, upon drying, a clear film is formed.

SHRINKAGE

The dehydration reaction shown in Table 6 causes shrinkage of the coating. The polymeric chains are drawn more tightly together. Chemical linkage occurs between the submicron particles and the adjacent polymeric chains.

The coating becomes denser by a decrease in thickness, or by a lateral shrinkage of the surface, or by a combination of both.

Figure 5 shows a sheet (1) with a coating (2) of thickness d_0. Because of the shrinkage of the coating (2), the sheet warped into a spherical shape having a radius r_2 to the coating. The initial length L_1 of the sheet is maintained at the center line of the sheet during its curvature to radius r_1.

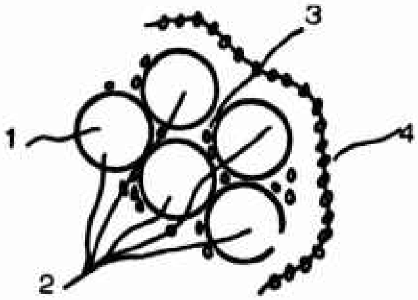


Figure 3. Case I Polymer Molecules Surrounding Particle Aggregates in a Particle/ Fluid Suspension.

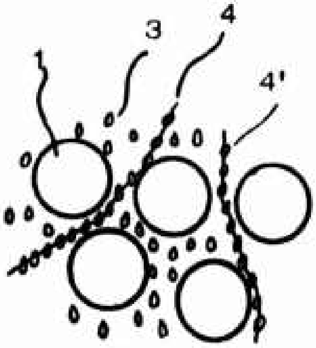


Figure 4. Case II Monomer and Polymer Molecules Between Individual Suspended Particles in a Particle/ Fluid Suspension.

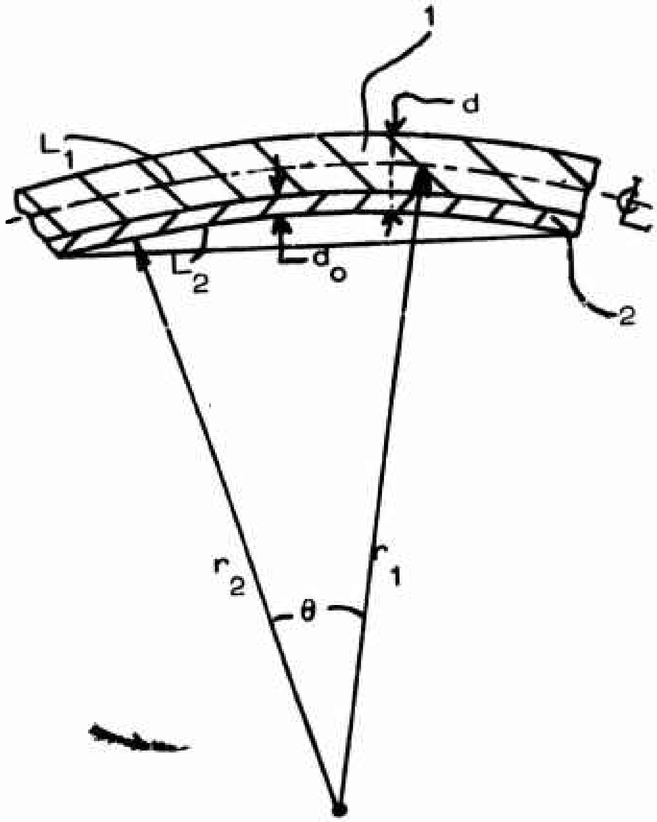


Figure 5. Spherically Curved Substrate and Coating.

The relationship between the length L_1 to the radius r_1 and the subtended angle θ is

$$L_1 = r_1\theta \qquad (1)$$

The relationship between the length of the coated surface L_2 to the radius r_2 of its surface and the same subtended angle θ is

$$L_2 = r_2\theta \qquad (2)$$

The percentage of shrinkage is given by

$$\%\ \text{shrinkage} = (L_1-L_2)/L_1 \qquad (3)$$

Substituting (1) and (2) into (3) putting $d = 2\,(r_1 - r_2)$ and $r = r_1$ and simplifying r_1 to r in the final equation,

$$\%\ \text{shrinkage} = 2\,(d/r)\,100 \qquad (4)$$

It is advantageous to apply the coating to a prestressed and prewarped plastic surface. This allows the coating to shrink laterally as the plastic is gradually relaxed, without introducing stresses which may cause rupture and crazing of the coating.

Figure 6 shows plastic sheet (1) in a stress fixture, prestressed opposite to the direction of shrinkage. The stress fixture comprises a ring (3), a rubber compression sheet (4), a pressure disk (5), and a spin shaft (6).

In operation, the plastic sheet is prestressed by turning the threaded disk (5) on the threaded clamp (3) to compress the rubber sheet (4). This warps the plastic sheet (1) to a radius r_1. The coating (2) is applied to the outer surface of plastic sheet (1) by spin-coating about the axis (6).

The fixture and the convex plastic sheet (1) with coating (2) are placed in an oven for 40 hours at 90° to 100°C. While the coating is dried and heated, the plastic is allowed to relax to a flat sheet as shown in Figure 7, permitting the surface coating to shrink as it undergoes the cross-linking.

As an example, a 3mm acrylic sheet (Plex II) coated with FA5 and No. 129c was held at a temperature of about 140°C. This sheet warped to a radius of about 300mm with the coating on the inside surface. From (4), the lateral shrinkage is about 2%. The strength of the coating was increased. Plastic sheets with coatings at least 2 microns thick, with about 2% shrinkage, were harder and more resistant to rupture under pressure and impact than the coatings which did not shrink.

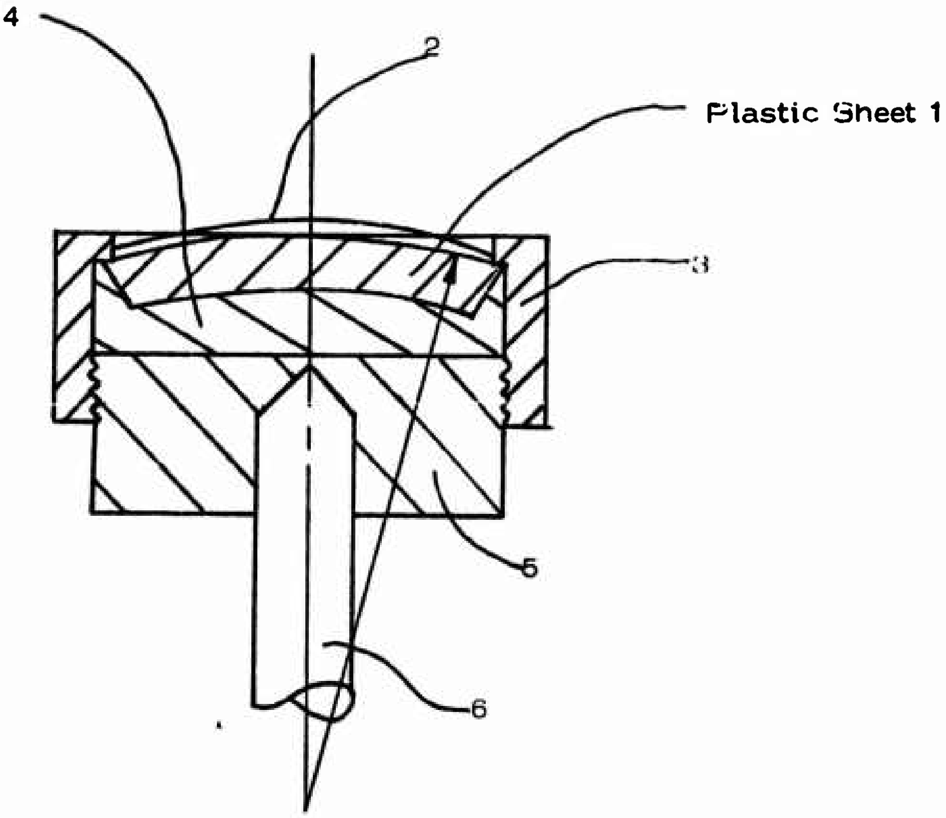


Figure 6. Device for Curving a Plastic Sheet and Spin-Coating the Sheet With Coating Before Relaxation.

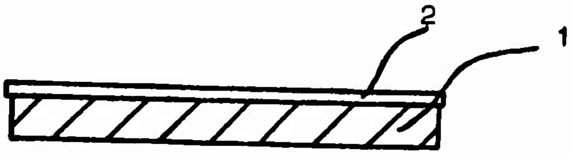


Figure 7. Plastic Sheet With Coating After Relaxation.

DEHYDRATION REACTIONS

Table 6 shows four different dehydration reactions occurring in the No. 129c composition (silica/pva 70/30) which result in coatings having different properties.

The Oxygen Cross-Link

Compositions I and II are respectively polysilicic acid and polyvinyl alcohol chains which lie in close proximity in the coating. Cross-linking occurs between adjacent hydroxyl groups with the formation of an oxygen bridge cross-linking the polysilicate and polyvinyl chains, shown at III.

The Silicon-Carbon Bridge

On further heating, adjacent hydrogen and hydroxyl groups on the polysilicate IV and polyvinyl chains V eliminate water, forming a direct silicon-carbon bond, shown as compound VI.

The formation of shortened silicon-carbon linkage results in a densification and hardening of the entire coating, which becomes more insoluble and less pervious to water.

Double Bonds

The color observed may be due to the unsaturated double bonding linkage known as a polyene, as shown in VIII, produced by the dehydration of adjacent H and OH groups on a polyvinyl alcohol chain VII, catalyzed by heat and the presence of an acid such as HCl. The dehydration occurs at greater than a critical temperature: ~90°C for coatings having greater than a critical thickness of about 2 microns. At a lower temperature, for example 60°C, the HCl escapes, the polyene structure does not form, and the silicon-carbon linkage VI is favored, on subsequent heating to 100°C. Thus, if the coating is heated at a temperature of 60°C or less, no color appears, even upon subsequent heating to a higher temperature.

Single and Double Bonds

Alternating single and double bonds may be produced along the carbon chain as shown at X.

Insolubilization

The cross-linking of the hydroxyl groups of the silica and the pva may not be sufficiently complete to prevent water penetration, particularly for boiling water. This water penetration softens the coating. The hardness reappears when the water is eliminated by heating. The softening is thus reversible. To eliminate the softening, the residual hydroxyl groups in the structure must be cross-linked with a water-insoluble and water-repellent composition, to fill the molecular voids which remain within the film structure.

Particle-Matrix Bonding

Submicron particles comprising alumina, zirconia, and silica all form hydroxyl groups in water. If such submicron particles are suspended in a water solution of polyvinyl alcohol and polysilicic acid coated on a substrate and heated for 4 hours at 100°C, oxygen bridge bonding will occur; on continuing at 100°C for more than 24 hours, direct Al-C, Zr-C, or Si-C bonding may also occur.

These bonds cause the particles to be chemically bonded to the matrix. The resulting composite coating exhibits hardness > 6 and becomes less pervious to water.

POROUS AND ABSORBED (POPAC) LAYER

A new layer structure (POPAC), unrelated to the composites described above, was discovered in the course of this work. The following describes initial work on this new structure.

A porous coating of silica/Alon 70/30 was prepared and applied to glass and plastic, producing a haze. When a drop of water or other liquid placed on this porous coating was absorbed, the coating became transparent; but, when the water or liquid evaporated from the pores of the coating, it again became hazy. A water-diluted 75/25 silica/pva coating over a porous 70/30 Alon/silica coating filled the pores and produced a permanently clear film. This principle may be employed to prepare other porous absorbed composite coatings which may have unique properties.

Referring to Figure 8, a porous and absorbed coating POPAC layer (3) is shown adhered to a substrate (1) having a surface (2), which optionally may have a primer coat. Two magnified views are shown in circles (4) and (5),which respectively represent two stages in the preparation of the POPAC layer. Particles (6) are hard particles such as Alon or silica and are shown at a magnification of 1 million; that is, particles having an average diameter of 150 Å.

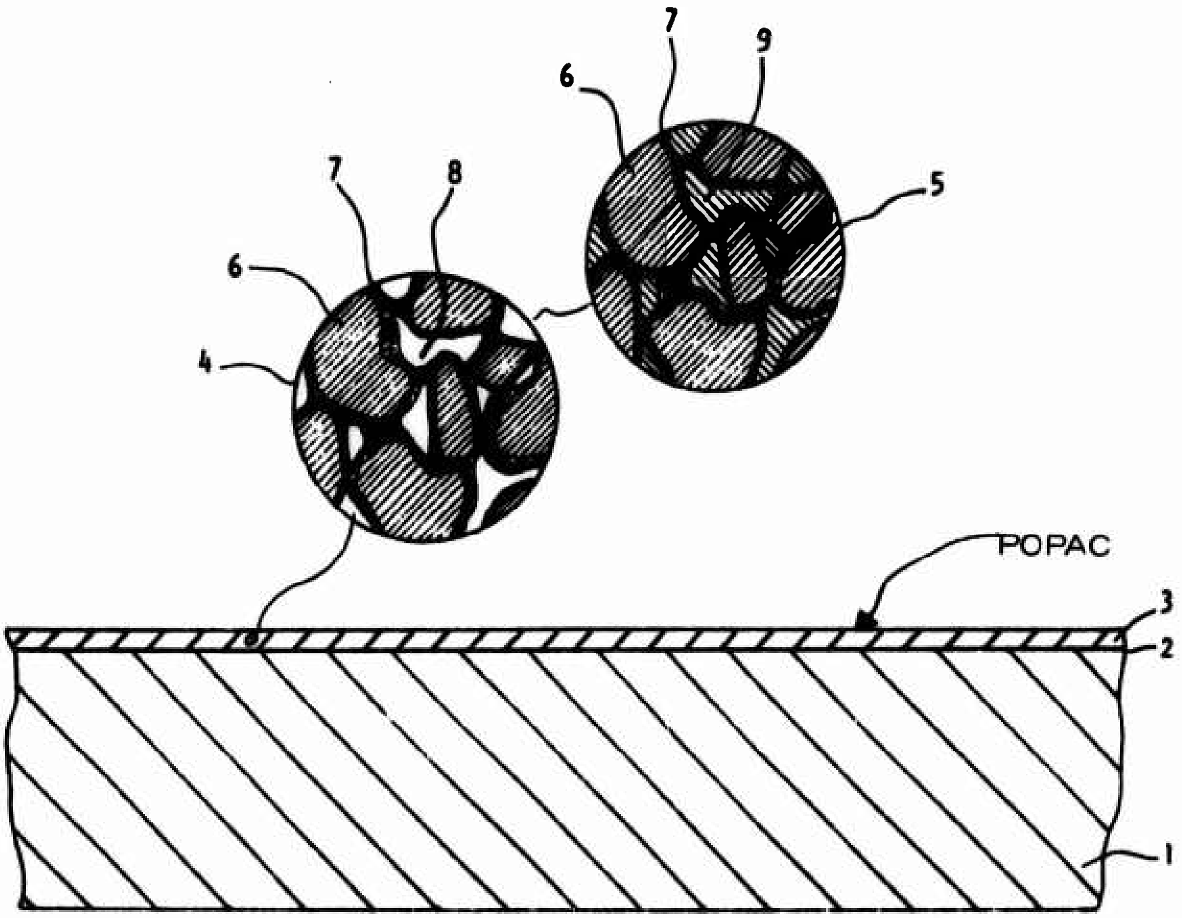


Figure 8. POPAC Layer.

In preparation of the POPAC layer, the particles (6) are suspended in a fluid, for example, water, containing a binder (7) which is a small proportion of the particle weight. The fluid suspension and binder are coated onto the surface (2) of the substrate (1), for example, by spinning or flow-coating, and are dried by heating to eliminate the fluid, thus leaving a thin binder (7) coating the particles and joining them at their contiguous edges, voids or interstices (8) remaining between the joined particles. These voids are submicron in size and have high capillarity; that is, a high absorptivity for fluids. During work on this contract, it was discovered that the porous coating in circle (4) would imbibe a hard polymeric solution, such as polysilicic acid/pva in water, which on subsequent drying filled the interstices (8) shown in circle (4) with the polymer (9) shown in circle (5); this, upon drying and heating, produced a superhard complex. This complex comprises superhard particles (6) such as submicron aluminum oxide held together with a flexible polymeric binder (7) and containing the hard polymer (9) filling the interstices (8), all components being chemically bound at their interfaces. In this example, a reaction occurs between hydroxyl groups at the surfaces of the aluminum oxide (aluminum hydroxides), the binder polymer (7), hydroxyl groups (as present on polyvinyl alcohol, polyvinyl formal, and/or inorganic polymers), and the hydroxyl groups on the interstitial compound (9). Upon heating, the proximate hydroxyl groups react, eliminating water, and the entire mass solidifies to form a superhard transparent coating, as illustrated within circle (5).

A porous layer was formed from about 60/40 to 90/10 submicron particles/polymeric binder. The interstitial absorbed coating was applied from a water solution of polysilicic acid/polyvinyl alcohol 75/25 or 70/30, and approximately 15% solids dissolved in water. During the stage shown in the figure within the circle (4), the coating appeared hazy; that is, it scattered light due to the interstitial voids (8). When this layer was wetted with water, it became transparent, but the haziness returned as the water evaporated. However, upon application of a water solution containing about 15% solids of polysilicic acid/polyvinyl alcohol (75/25), the coating became transparent and remained so after the fluid was evaporated; and a superhard POPAC coating resulted. This is an example of the general physical principle illustrated in Figure 8.

Other porous absorbed composite coatings can be prepared on this principle. These coatings should have unique properties.

METHODS AND APPARATUS

DISPERSER

A Gaulin Submicron Disperser was used to disperse submicron particles in a fluid. As an example, a 10% suspension of submicron particles in water was circulated 10 times through the device at 8,000 to 10,000 psi to obtain an excellent dispersion.

CENTRIFUGE

A Sorval Centrifuge was used to centrifuge the fluid dispersion of submicron particles to obtain a sediment in the slot between 9,000 and 10,000 rpm. This formed a transparent particle water gel. Transparent gels were obtained with all the particles listed in Table 2.

SPIN COATER

The coatings were applied by a spin coat method. The coating thickness is a function of the fluid viscosity, rpm and time. The fluid viscosity is a function of the percentage of solids of the fluids. The preferred rpm varied from 500 to 3,000 and the corresponding times decreased from 30 to 5 seconds, producing, when dry, a coating of 1 to 7 microns thickness. Smaller rpm increases the coating thickness, but the coatings may lack uniformity. Greater rpm decreases the coating thickness. Very uniform coatings were produced in the preferred range.

COATING LARGE CURVED PANELS

Large-area flat or curved panels may be coated by a spin coat method, a gravity flow coat method, or a combination of these methods. In this work only the spin coat method was used.

Marks Polarized Corporation has successfully spin-coated large curved panels about 48" in diameter. This procedure is an established fact. There does not appear to be a limitation on the size of the panel to be spin-coated so long as the maximum slope of the surface relative to the horizontal does not exceed 45°. We have coated flat windows by a gravity flow coat process (size about 14' x 8'). Very large curved panels can be coated by using a large spinner. A combination of flow coating and spin coating may be used.

Coating thickness may be measured in two ways:

<u>Method 1</u> With a micrometer measure the thickness of

(1.1) the substrate = d_s

(1.2) the substrate plus the coating = $(d_s + d_c)$

(1.3) the thickness of the coating: $d_c = (1.1) - (1.2)$

<u>Method 2</u> Weigh

(2.1) the substrate = w_s

(2.2) the coating plus the substrate = $(w_c + w_s)$

(2.3) Then the weight of the coating $w_c = (2.2) - (2.1)$

(2.4) Divide by the area of the substrate A to obtain the weight of the coating per unit area = (w_c/A)

(2.5) The density δ of the coating is measured from the weight and displacement of the coating, removed from a substrate such as sheet Mylar, to which the coating does not adhere.

(2.6) The coating thickness is: $d_c = w_c/A\delta$

Method 1 was used to calibrate thickness; then Method 2, through (2.4), was used to measure d_c vs. w_c/A. Subsequently, thickness can be computed from w_c/A.

APPROACH

SUBMICRON-HARD PARTICLE-POLYMER COMPOSITES

Known particles with a hardness of 7 or more have been listed in Table 1, with other pertinent properties, particularly color. Only the diamond has a hardness (15) greater than alumina (9) and is always colorless, with the exception of pure silicon carbide which has a hardness of 13. However, pure silicon carbide is not available commercially. At the present time,

TABLE 1. COMPARISON OF HARDNESS VALUES OF VARIOUS MATERIALS ON MOH AND KNOOP SCALES

Substance	Formula	Hardness		Color	Crystal Form	Refractive Index	Density (gm/cm^3)
		Moh	Knoop				
Silicon Dioxide as Quartz	SiO_2	7	820	Colorless	Hexagonal	1.54– 1.55	2.653 – 2.660
Titanium Dioxide (Rutile)	TiO_2	>7	–	Colorless	Tetragonal	2.616	4.26
Alumina	Al_2O_3	9	2100	Colorless	Hexagonal	1.760	3.97
Titanium Carbide	TiC	–	2470	Grn. Met.	Cubic	–	4.93
Silicon Carbide	SiC	13	2480	Colorless to Black	Hexagonal or Cubic	2.654 2.697	3.217
Aluminum Boride	AlB_2	–	2500	Copper Red	Hexagonal	–	3.19
Boron Carbide	B_4C	14	2750	Black	Rhombic	–	2.52
Diamond	C	15	7000	Colorless	Cubic	2.4173	3.51

TABLE 2. CHARACTERISTICS AND SOURCES OF SUBMICRON-HARD PARTICLES

Trade Name	Description	Chemical Name and Formula	Moh[1] Hard-ness	Shape	Size (Å)	Electrical Charge
Alon®	fumed alumina powder	Aluminum oxide, Al_2O_3	6	irregular sphere	200	+
Dispal M	dispersible alumina powder	Aluminum oxide, Al_2O_3		irregular sphere	100	+
Cab-O-Sil	fumed silica powder	Silicon dioxide, SiO_2	6	irregular sphere	100	−
Baymal® Sol-Al^{tm}	boehmite alumina powder	Aluminum hydroxide, AlOOH		needle	1000 × 50	+
Attagel®50	attapulgite powder	Magnesium aluminum silicate $(MgO)(Al_2O_3)(SiO_2)$		needle	1400 × 100	−
	α-silicon carbide	Silicon carbide, SiC	13	needle		

TABLE 2. - Continued

Trade Name	Description	Chemical Name and Formula	Moh[1] Hardness	Shape	Size (Å)	Electrical Charge
Ludox® 130M	aluminum hydroxide coated silica suspended in water	$SiO_2 + Al_2O_3$		sphere	160	+
Colloidal Zirconia	zirconium dioxide suspended in water in a 20% concentration	$ZrO_2 \cdot xH_2O$		monoclinic	50 to 250	
Nalco E 119	aluminum formate coated silica sol in water	$Al(COOH)_3$ on SiO_2		sphere	200	+
Nalcoag® 1034 A	colloidal silica suspended in water in 34% concentration	Silicon dioxide, SiO_2		sphere	160 to 220	-
Nalcoag® 1115	colloidal silica suspended in water in 15% concentration	Silicon dioxide, SiO_2		sphere	40	-

commercial grades are always colored because of the presence of impurities. Consequently, as present, only the diamond appears better than aluminum oxide,and the diamond may be precluded from all but a few specialty uses because of expense.

Various submicron particles comprising spherical particles and/or rod-shaped whiskers are available commercially as powders and particle-water suspensions and are listed in Table 2. Some sources were known at the start of the project, but many were discovered later.

When not previously dispersed, the particles of various sizes and shapes were suspended in a fluid using a disperser or homogenizer.

The particles in suspension were separated in a high-speed centrifuge into various submicron sizes less than 500 Å to produce a transparent particle-liquid paste.

This paste was mixed in various proportions with a transparent polymer and solvent and was applied as a coating to a transparent substrate, and the solvent was evaporated to form a superhard polymer-particle composite layer.

The physical properties of superhard composite polymers were determined by varying the polymer composition and the concentration of particles. Particle shape and size were determined from the data obtained from manufacturers and, in the case of one composition, from electron microscope pictures.

Compositions containing irregular and rod-shaped submicron particles were prepared. The work started with irregularly shaped submicron particles mixed in various proportions with polymers to produce superhard transparent sheets.

The superhard transparent materials produced were evaluated for their optical and physical properties by the test program hereinafter described. The characteristics of superhard transparent plastic candidate compositions were identified and analyzed for abrasion resistance suitable for application to helicopter transparencies. The work included studies of the effects of particle type, shape and size; concentration; polymer composition; chemical reactions; temperature and time; film thickness; methods of manufacture for application to contoured canopies; and hardness on the Moh scale (5 was acceptable, attained, and exceeded). The visible optical transmission and haze were the same as the plastic sheet substrate with or without these coatings.

Most of the evaluations made were on glass, Plex II (cast) and stretched Plex. The polycarbonate samples did not arrive until later in the program; subsequently, coatings were made and submitted on polycarbonate. Comparison of the coatings prepared on polycarbonate and Plex showed no apparent difference, except that the surface of the polycarbonate was subcoated with a different, thin (1-micron) subcoat; namely, 5% Formvar, 92% acetic acid, and 3% diacetone acrylamide. No significant difference was found in the evaluations of the test specimens of different substrates for coatings 4 microns or more in thickness.

Five test specimens of each of the four selected compositions were prepared. The test specimens were 2-5/8"-square flat panels comprising cast acrylic, stretched acrylic and polycarbonate panels.

MOH HARDNESS vs. COMPOSITION IN SYSTEM 1: SILICA/PVA/ALON

The Moh hardness was obtained by abrading the surface of the coatings with various materials of known Moh hardness, as shown in Table 3. Figures 9 through 17 show Moh hardness vs. silica/pva/Alon.

Moh hardness tests were made on coatings of pva/Alon with no silica; silica/pva with no Alon; silica/Alon with no pva; and silica/pva/Alon. This hardness data was utilized in completing the triangle chart of composition of the system. The Moh hardness of these compositions is summarized on the triangle graphs in Figures 9 and 10, which show lines of constant hardness. Superhard (Moh > 5) coatings were produced over the range of compositions shown. A region bounded by the lines AB and BC contained the hardest compositions in this system, which had a Moh hardness > 6; that is, hardness equal to or better than glass. The thickness of the coatings was about 4 microns. The thickness was measured using Methods 1 and 2 previously described. For initial evaluations, tests were performed on coatings spun onto glass slides 2-5/8" square. Subsequently, the best compositions were spin coated onto cast Plex II of 2-5/8"-square size.

Hardness vs. Silica/Alon

Figure 2 shows Moh hardness vs. silica/Alon. The coating was heated to 140°C for 2 hours. At 100% silica, the curve starts at a Moh hardness of about 4.8. As the Alon increases to 20%, the hardness increases slightly to 5. As the Alon increases to 22%, the hardness rises rapidly to a peak of 6.5. As the Alon exceeds 22%, the hardness rapidly decreases to 4.5 at 35% Alon. All silica/Alon compositions are clear except those coatings from compositions 60/40 to 75/25, which are hazy

TABLE 3. MOH HARDNESS FOR VARIOUS MATERIALS COMPARED WITH ERASER TESTS

Moh Hardness	Material Equivalents			Eraser Marking
	A[1]	B[1]	C	D
1	Talc			
1.5	Tin	Lead		
2	Cadmium	Magnesium		
2.5	Zinc	Plex	Polyvinyl Alcohol	Heavy
3	Calcite	Copper	Abcite®	Medium
3.25	Barite		CR-39®	Slight
3.5	Marble		Marks 126	Very Slight
4	Fluorite	Phosphor Bronze		
4.5	Iron			Faint
5	Manganese			None
5.5			Steel Wool[1]	
6	Orthoclase	Hematite Pumice	Glass Sheet[1] Alon Alumina (fumed)	
7	Quartz			
8	Topaz	Chromium		
9	Alumina			
12	Alumina (fused)	Aluminum Oxide		
13	Silicon carbide			
14	Boron carbide			
15	Diamond			

and porous. With the further increase of Alon above 75%, the coating is powdery and soft enough (Moh 1) to be wiped away.

Hardness vs. pva/Alon Composition

Alon-water gel and pva in water were mixed in various percentages, coated onto glass, heated to 140°C for 2 hours, and measured for hardness. The results, plotted in Figure 11, show that the hardness was nearly constant from 0 to 10% Alon, increased to a peak of 3.8 in the range of 50% to 60% Alon, and decreased rapidly to about 2 at 75% Alon. At greater than 70% Alon, the coatings were hazy and porous and may be useful in the production of POrous Particle Absorbed Coatings, now termed a "POPAC" layer.

Hardness vs. Silica/pva

Figure 12 shows Moh hardness of the system pva/silica, with no Alon. All of these compositions are clear. Film was heated for 1 hour at 140°C. For compositions from 100/0 to 0/100 silica/pva, the coatings are clear. The hardness is about 4.8 for 100/0 (pure silica), increases to a peak of 5.5 Moh at 75/25 silica/pva, and then decreases to 2.

Composition No. 129c, comprising 70/30 silica/pva, forms a stable, flexible, noncrazing, clear and smooth film which, after 2 hours heating at 100°C, has a Moh hardness of about 5.2. Composition No. 129c is a superhard flexible film which shows excellent promise. The coating thickness is 4 microns.

Hardness vs. Alon/Silica/pva

Figures 13 through 17 show Moh hardness vs. percent Alon/percent (pva + silica) for various constant % pva from 5% to 50%.

MOLECULAR WEIGHT OF POLYMER

Polymers of Elvanol® polyvinyl alcohol were tested in films having the composition 70/30 silica/pva. The characteristics of these polymers are shown in Table 4.

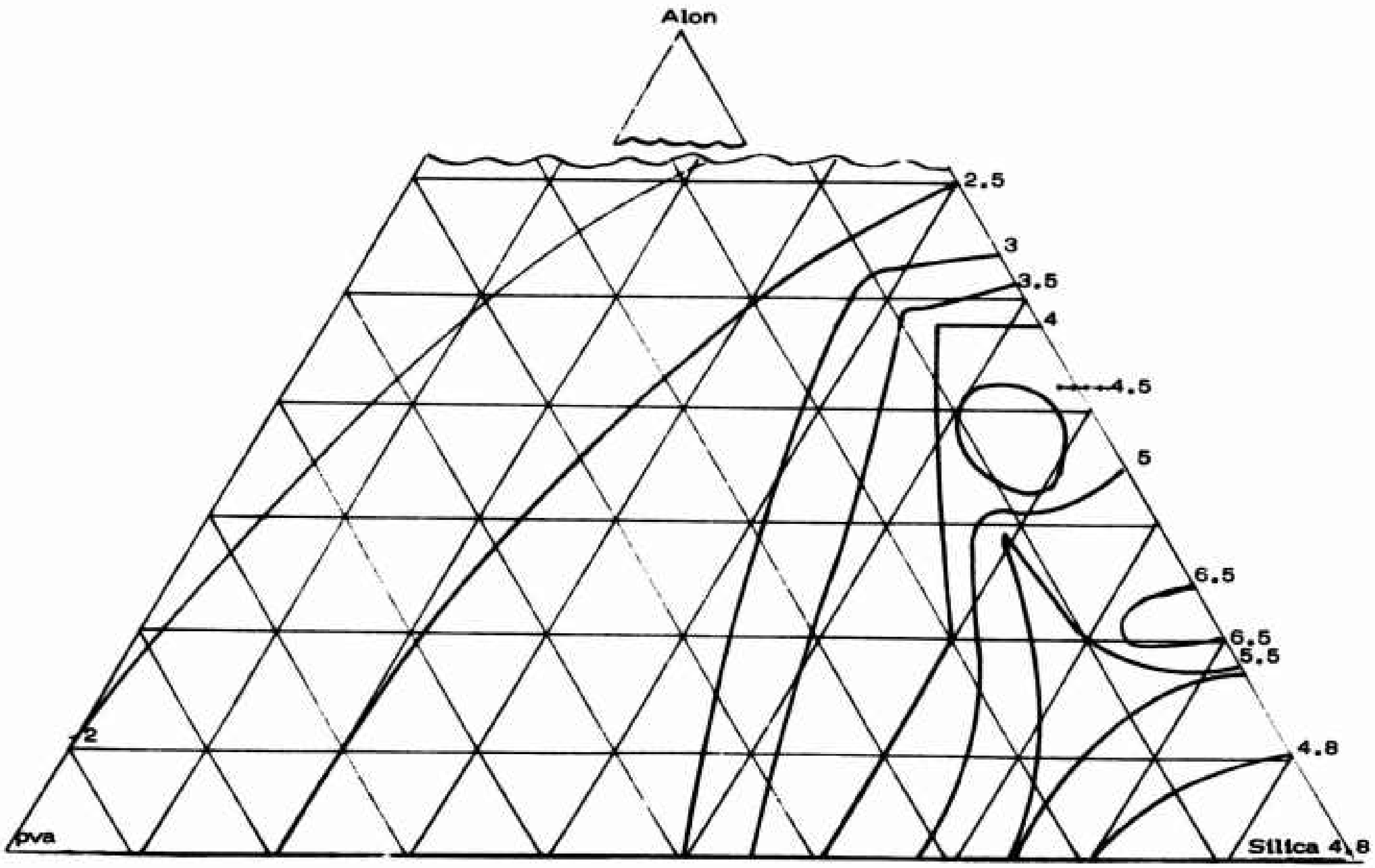


Figure 9. Lines of Constant Moh Hardness vs. Composition.

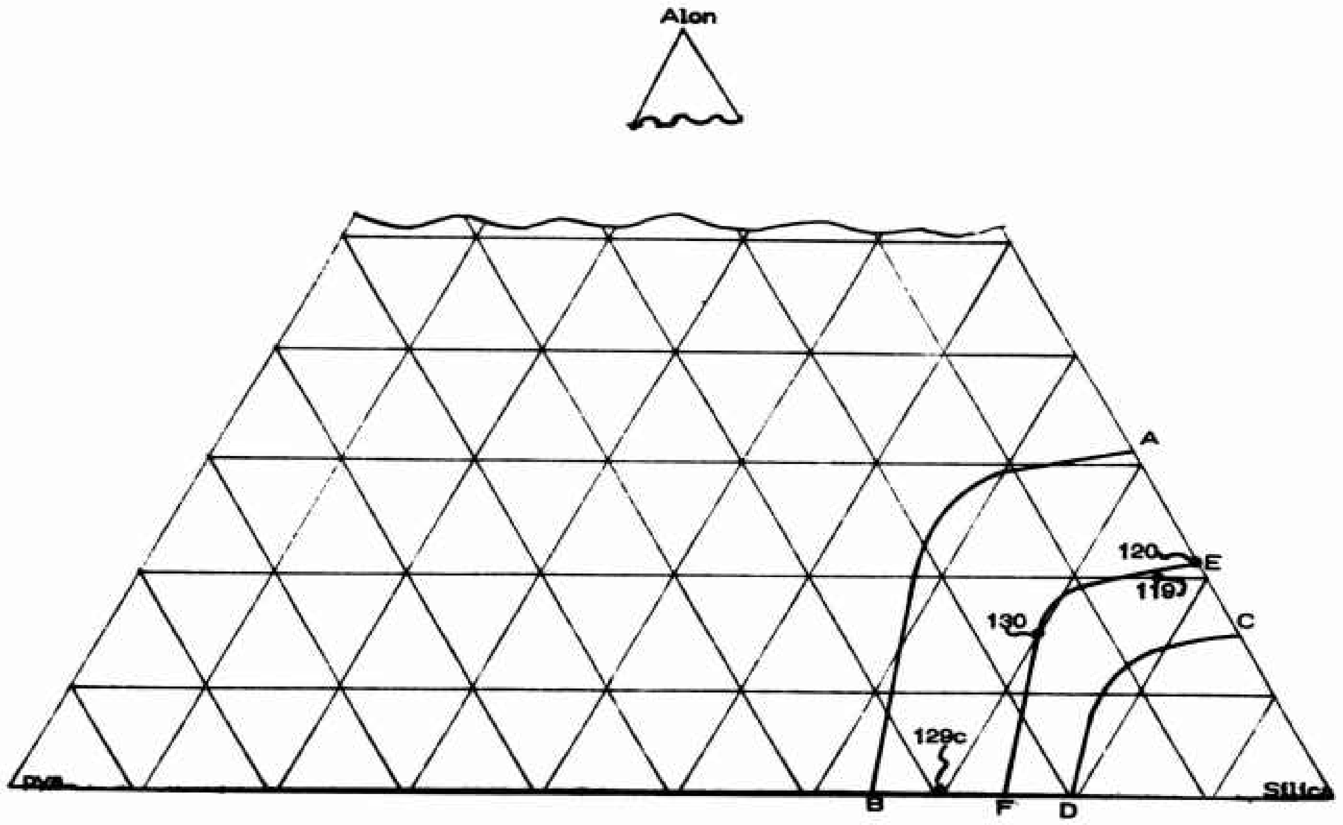


Figure 10. Optimum Compositions.

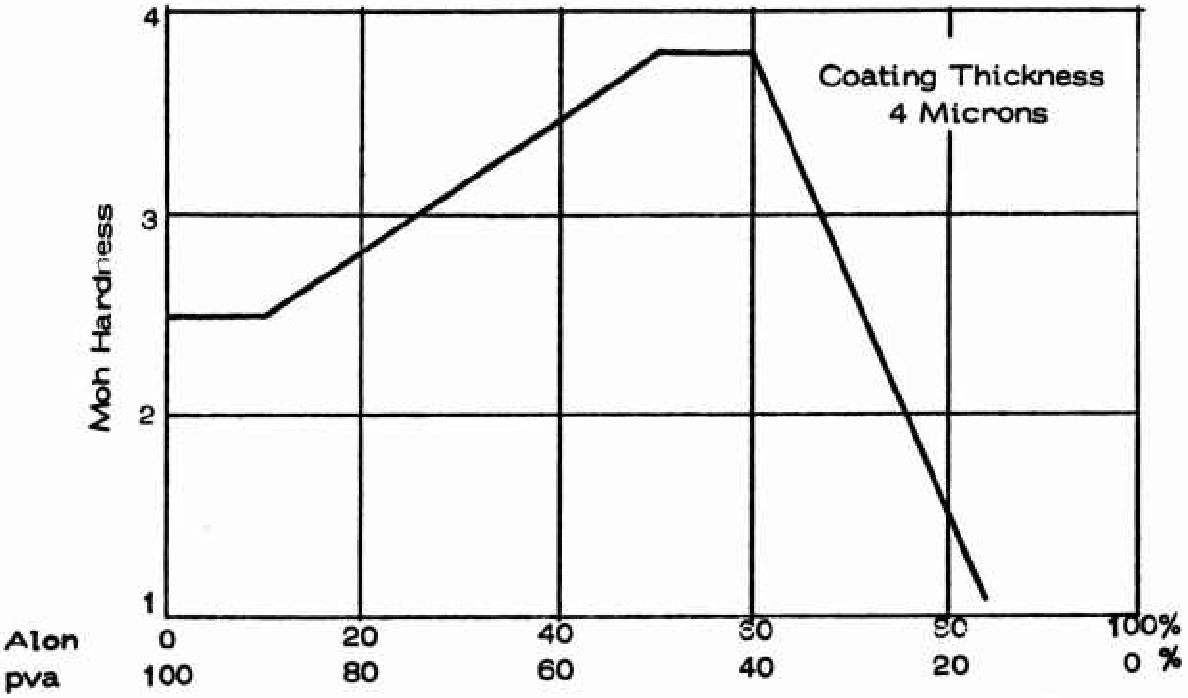


Figure 11. Moh Hardness vs. % Alon/% pva Heated to 140°C.

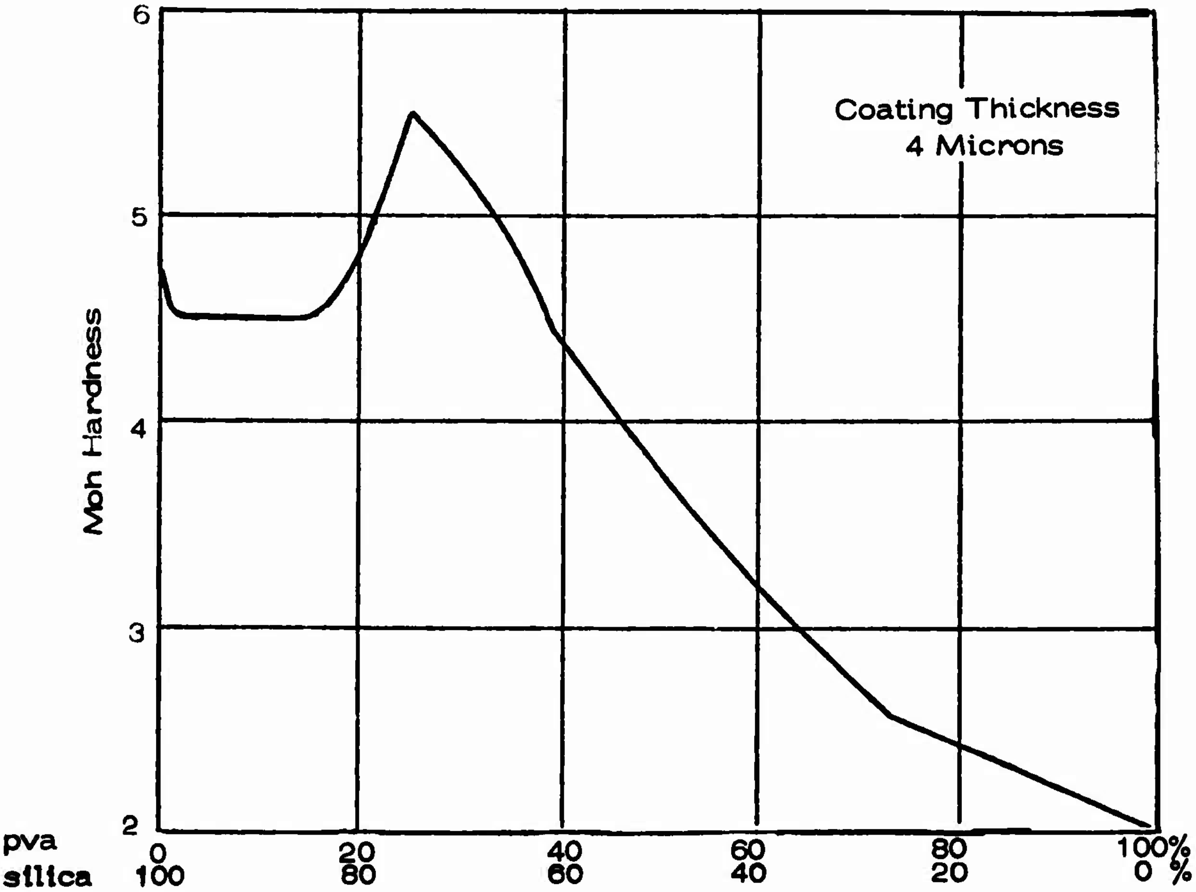


Figure 12. Moh Hardness vs. % Silica/% pva.

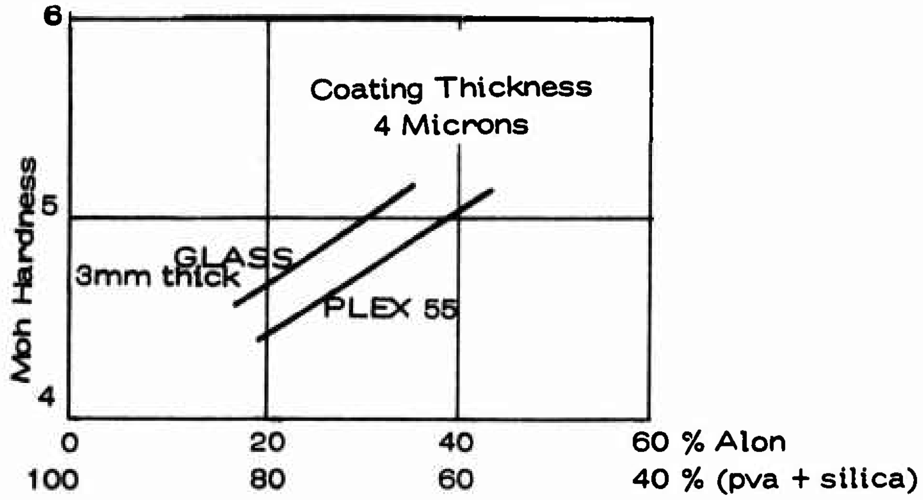


Figure 13. Moh Hardness vs. % Alon/% (pva + silica) for 5% Constant pva Heated to 95°C for 4 Hours.

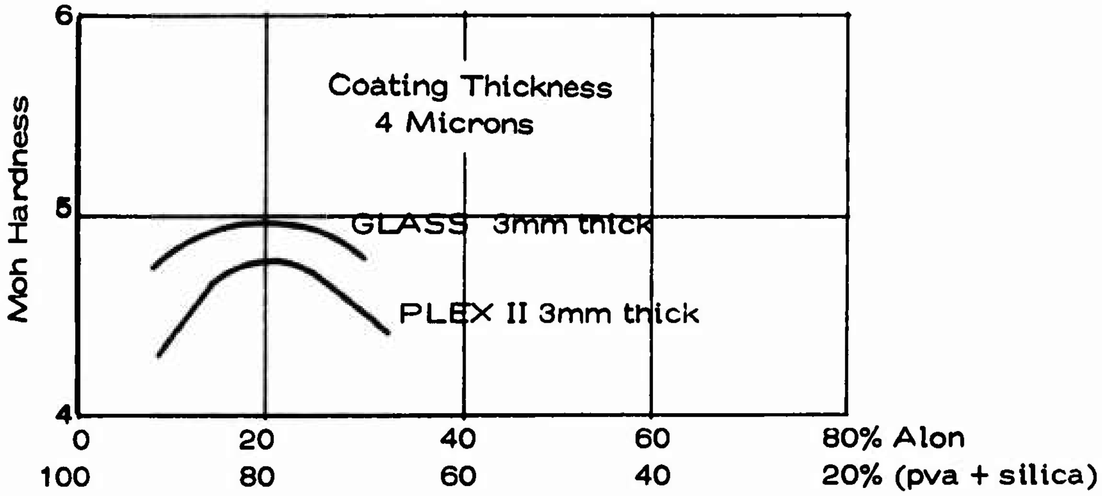


Figure 14. Moh Hardness vs. % Alon/% (pva + silica) for 12% Constant pva Heated to 95°C for 4 Hours.

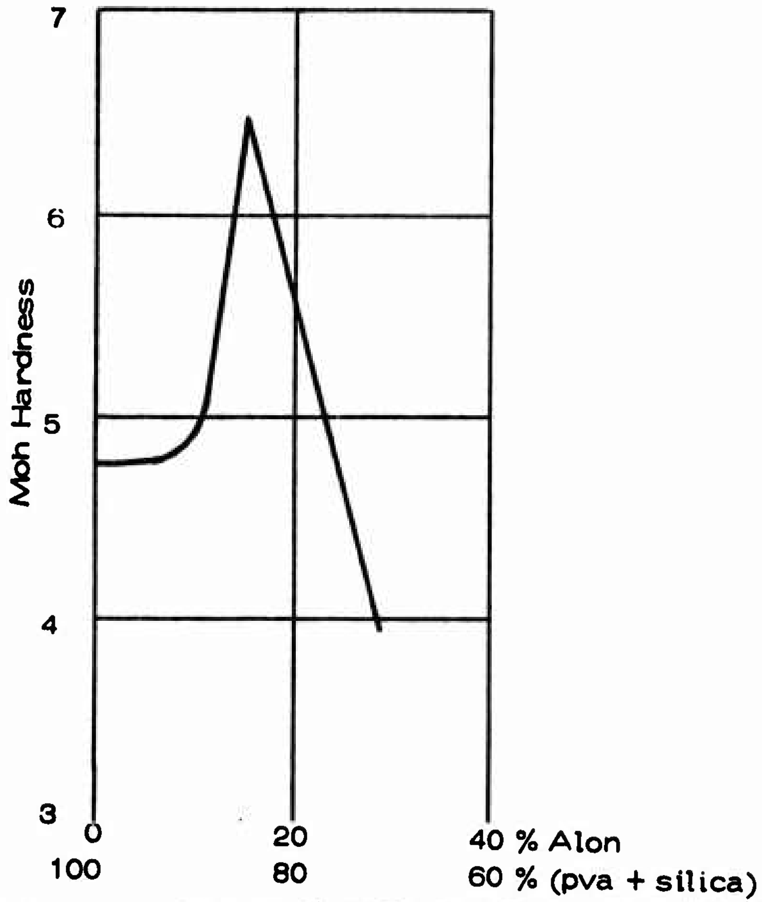


Figure 15. Moh Hardness vs. % Alon/% (pva + silica) at Constant 15% to 20% pva Heated to 140°C on Glass.

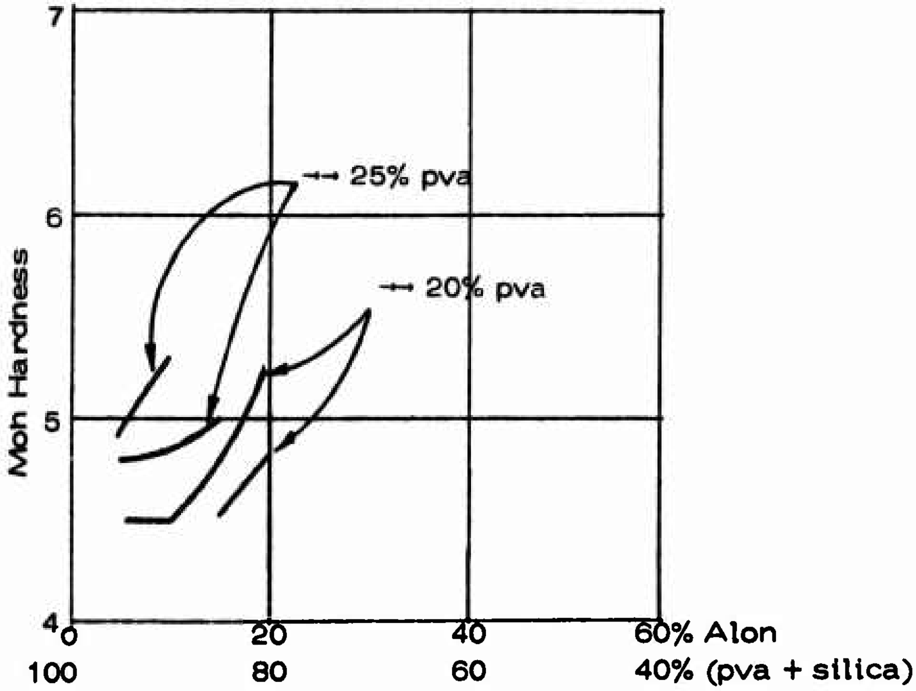


Figure 16. Moh Hardness vs. % Alon/% (pva + silica) for Constant 20% and 25% pva Heated to 100°C on Plex II.

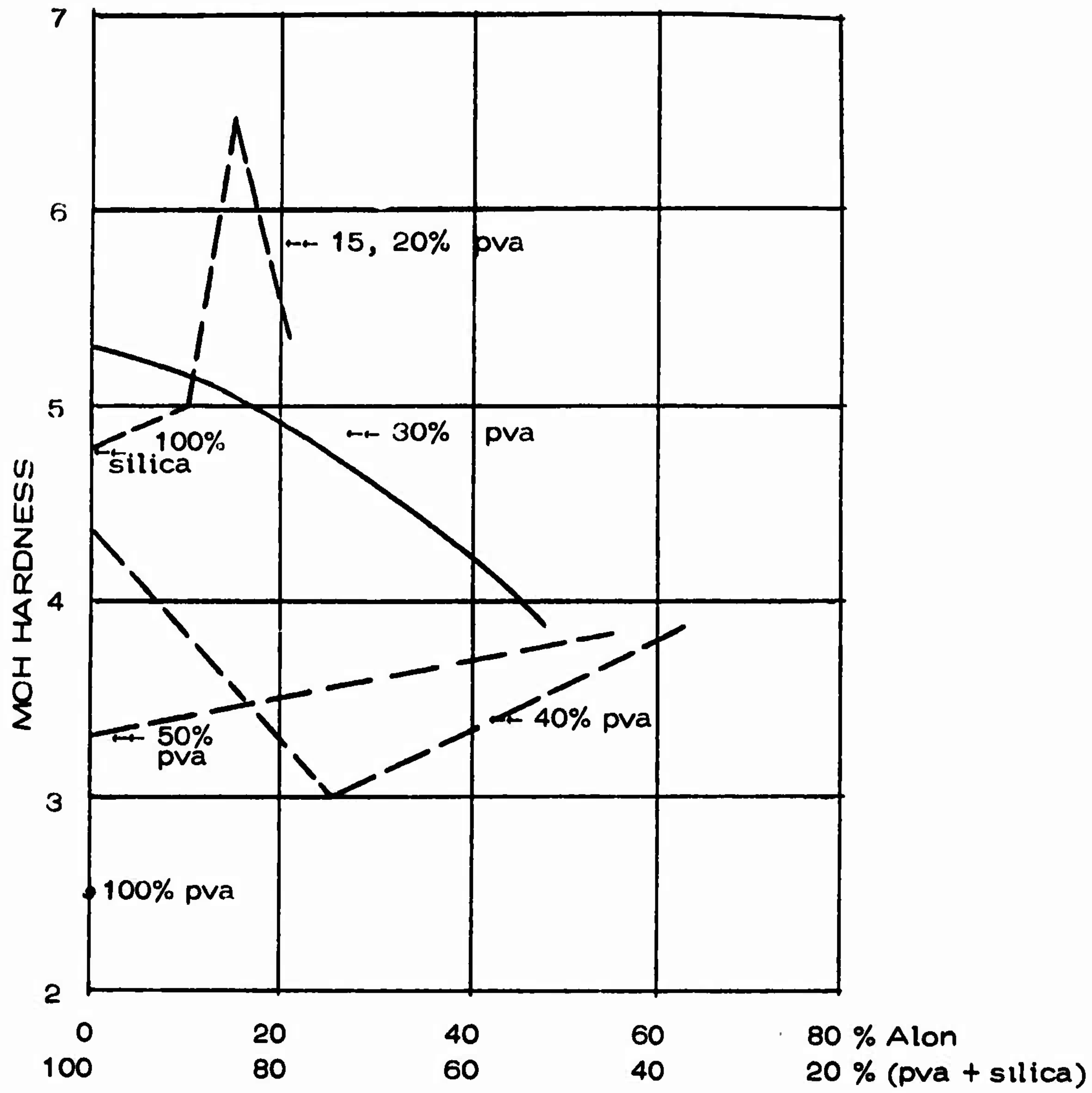


Figure 17. Moh Hardness vs. % Alon/% (pva + silica) for Constant pva Heated to 105°C for 1 Hour and 140°C for 6 Minutes on Glass.

TABLE 4. CHARACTERISTICS OF POLYVINYL ALCOHOL POLYMERS

Grade of Elvanol®	% Hydrolysis	Molecular Weight
72-60	99+	High
71-30	99+	Medium
70-05	99+	Low
50-42	87	Medium

The low-molecular-weight polymer lacked strength, and the highest-molecular-weight polymer was slightly softer than the medium-molecular-weight polymer. The fully hydrolyzed (99+%) medium-molecular-weight polymer 71-30 was about the same as the partially hydrolyzed (87%) medium-molecular-weight polymer as to hardness and flexibility. Polymer 71-30 was selected as the best fully-hydrolyzed medium-molecular-weight polymer.

ADDITIVES

Additives are reactive materials mixed in a relatively small proportion into coating compositions to increase hardness, decrease water permeability and curing time, improve adhesion, and prevent epitaxial crazing. The additives must be compatible with polysilicic acid and polyvinyl alcohol, that is, with System 1 compositions. Those listed as compatible in Table 8 show promise for this purpose. The list is not exhaustive, but it is suggestive of the many possibilities. Among the compositions showing promise were hexamethoxymethylmelamine (Cymel®) and accelerators such as 1010.

Various organic titanates were mixed into polysilicic acid solution. Only a small amount of organic titanate, about 0.25%, could be added while still retaining clarity of the fluid and enabling formation of a clear film. Larger amounts produced cloudy suspensions or cloudy, solid, or oily precipitates.

Diacetone acrylamide (DAA) is N-(1,1 Dimethyl-3-oxobutyl) acrylamide. It reacts with hydroxyl groups and with various acrylic monomers such as methacrylic acid.

The composition silica/pva/DAA 70/25/5 heated for 12 hours at 65°C and 20 hours at 90°C spun onto a Plex II surface with primer FA5 at 850 rpm for 13 seconds produced a hardness of about 6 with excellent clarity and no crazing.

Over the major portion of the contract period, all coatings were prepared with a 2-hour heating time at various temperatures and at substantially the same thickness of about 4 microns. The hardness evaluations were made on these coatings. Coatings 119, 120, and 130 were all harder than 129c; that is, about 6.5, compared with 5.0 (see Table 9, column A, under "Hardness"). Later, it was found (see Figure 21) that on heating for longer times, for example, 40 hours, composition 129c increased in hardness to about 7. The coatings which had been heated for only 2 hours showed water-permeability.

This work was commenced to decrease the water permeability of coating compositions. Titanium has a valence of 4 and a residual valence of 5. Isopropyl titanate vapor reacts with extreme rapidity with water or hydroxyl groups, splitting off isopropyl alcohol, which evaporates, leaving a titanium dioxide as an integral coating or as an O-Ti-O cross-link. Any water present will also release isopropyl alcohol. When a coating is exposed to isopropyl titanate vapor, the vapor penetrates voids in the coating and reacts with available hydroxyl groups on the chains or with residual water which may be present. Subsequently, when this treated film is heated, the residual isopropyl alcohol evaporates, and the film is solidified and made impervious to further water penetration, with an increase in hardness. Coating No. 129c was heated for about 4 hours at 100°C and exposed to the vapors of isopropyl titanate at 70°C for 1, 5, 10 and 30 minutes; it was then heated for 2 hours at 100°C. All samples formed clear films with improved water resistance. The purpose for their exposure to isopropyl titanate vapor was to decrease their water-absorbancy. However, prolonged heating time rendered coating No. 129c impervious to water, and the isopropyl titanate vapor treatment became unnecessary.

Most of the results, graphs and tables apply to the work initially done with the 2-hour heating period. It is recommended that this work be repeated for longer time periods so that the same range of compositions can be studied after they have undergone a maximum cross-linking, which will result in advantageous properties, and that this work be done with rod-like hard particles rather than sphere-like hard particles. No further evaluation was made of this approach, which was superseded by the simpler procedure of increasing the heating time to greater than 24 hours at 100°C.

SYSTEM 2: PHOSPHORIC ACID/SILICA/PVA

Phosphoric acid is miscible in all proportions with water, polysilicic acid and polyvinyl alcohol, forming a transparent coating upon evaporation of the solvent and heating. Without Alon, no coagulation occurred with any proportion of phosphoric acid. Figure 18 shows Moh hardness vs. percentage of phosphoric acid and (SiO_2/pva) constant at 70/30. The coating hardness decreases from about 5.2 Moh at 0% phosphoric acid to 3.6 Moh at 55% phosphoric acid. For not more than 7% phosphoric acid, the Moh hardness is greater than 5.

An Alon/silica/pva (No. 119) 20/75/5 coating composition coagulated to a thick paste and could not be coated when the phosphoric acid exceeded about 0.3%.

Phosphoric acid reacts with Alon, forming an aluminum phosphate bond. Phosphoric acid and polysilicic acid, when heated, react to form a phospho-silicate glass. Phosphoric acid reacts with the hydroxyl bonds of organic polymers. Silica/phosphoric acid formed clear coatings. One hundred percent silica did not craze and had a hardness of 4.8 Moh. The addition of 1 to 6% phosphoric acid caused crazing and softened the coating.

SYSTEM 3: ALON/POLYSILICIC ACID/BORACIC ACID

Boracic (boric) acid dissolves, 6% in water and 20% in methanol, at about 25°C. The dissolved boric acid is miscible with polysilicic acid and Alon in water and alcohol. Polyvinyl alcohol coagulated when boric acid-water was added and hence could not be used in System 3 coatings.

The composition boric acid/polysilicic acid/Alon appears to be compatible in all proportions, forming a clear, hard coating on evaporation of the solvent. Two compositions of SiO_2/Alon/boric acid 138A,B: 84.5/13.9/1.6 and 96/0/4 were heated to 100°C for 30 minutes. These were clear, but were soft and crazed.

Referring to Systems 2 and 3, phosphates and borates are known to form glasses with silicate. Systems 2 and 3 were investigated in an attempt to form coatings which were related to these known glasses. It was intended that the phosphoric acid or boracic acid replace the polysilicic acid, in effect, to form a phosphate or borate glass coating with the pva polymer. While these compositions formed clear films, they were not as water-impervious or as hard as those formed with silica. It was intended to include Alon in the event that these films had proven advantageous.

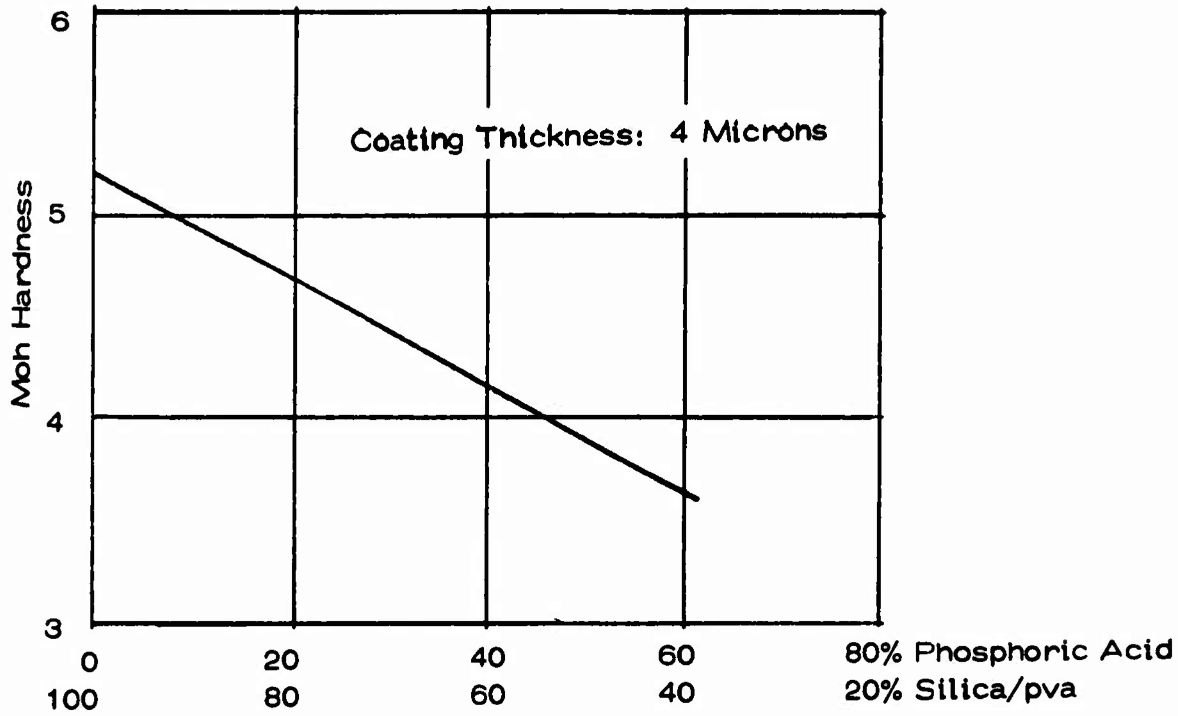


Figure 18. Moh Hardness vs. % Phosphoric Acid and % Silica/pva (70/30) Heated to 105°C for 30 Minutes and 125°C for 15 Minutes on Glass.

SYSTEM 4: ALON/SILICA/CYMEL - MOH HARDNESS vs. COMPOSITION IN THE SYSTEM

The compositions of System 4 were investigated following initial determination of the compatibility of various materials with silica, with the results given in Table 5. Cymel was chosen because it has six sites per molecule capable of forming cross-links with hydroxyl groups on pva and silica.

These tests were made using the 2-hour heating period. Although results were promising, further work was not done with Cymel since composition No. 129c was selected, making further work with Cymel unnecessary.

Table 5 shows the results for films coated onto Plex and glass heated to about 100°C for 2 hours. Cymel was found to form excellent hard, clear coatings with polysilicate and Alon, which adhered to a primer coating FA5 on a Plex substrate, and directly to glass. Composition No. 153 was found to be the best of this series.

OTHER SYSTEMS

A source was found for zirconium dioxide ZrO_2H_2O, comprising submicron particles about 150 Å in diameter.

Submicron particles of titanium dioxide were obtained. Although the literature reported a 300 Å particle size, not enough submicron particles could be obtained small enough to make a clear gel.

Coatings made from compositions in the system silica/pva/submicron silica particles were tested (Ludox).

Tests were made with zirconium dioxide and with Ludox (silica). Zirconium dioxide is available as a zirconium hydroxide spherical gel particle, and not as a solid crystalline hard particle. Coatings containing this material were clear, but the hardness was less than 5. Coatings were also prepared with Ludox (silica). These particles were spherically-shaped. While the films produced were clear, the hardness was generally less than 5. Because the particles were spherical and not needle-like, this material was not further considered.

TABLE 5. % SOLIDS IN SYSTEM ALON/SILICA/CYMEL VS. TEST RESULTS

Test No.	151	152	153	154	155
Silica	74	74	74	74	74
PVA	25	24	20	15	5
Cymel®	0	1	5	10	20
1010	1	1	1	1	1
TOTALS	100	100	100	100	100
Compatibility	E	E	E	P	X
Hardness	4.8	4.8	4.9	5.2	-

Key:
P = Partial Compatibility
E = Excellent Compatibility
X = Incompatible

Silica Particles

A clear paste was made from silica (Cab-O-Sil) by dispersing it in water and centrifuging at 9,000 to 10,000 rpm. A commercial source was found for submicron particles about 200 Å in diameter suspended in water.

Hydrophobic Silica Particles

To gain experience with hydrophobic particles, and to facilitate a study of their properties, a hydrophobic coated submicron silica, commercially available, was utilized in the foregoing tests. These particles have a diameter of 70 Å and are normally available as aggregates of particles.

It was found that they form excellent transparent gels in chlorinated hydrocarbons such as carbontetrachloride or 1,1,2-trichloroethane. More important, a transparent gel is formed with methyl methacrylate monomer, vinyl acetate monomer, and probably a variety of other monomers. This occurs even if the particle aggregates are not first homogenized.

Hydrophobic vs. Hydrophilic Particle Matrix Bond Strength

Comparison test results were obtained on the hardness and cohesiveness of hydrophobic coating compositions containing silica/pva/submicron particles or hydrophilic particles. Tests were made with submicron hydrophilic particles comprising silica and hydrophobic coated silica. Compositions containing hydrophilic particles were found to form strong cohesive films when cast from water or other polar solvents; but compositions comprising hydrophobic particles in nonpolar solvents were found to form soft noncoherent films which readily crumbled when subjected to abrasion.

Needle-Shaped Particles

Commercial sources for two submicron needle-shaped crystalline particles were found. These were Baymal® and SOL-AL®, submicron needle-shaped crystals of aluminum hydroxide, $AlO(OH)$, about 1000 Å long and 100 Å in diameter, and Attagel® 50, submicron needle-shaped crystals of aluminum magnesium silicate, $AlMgSiO_3$, about 1400 Å long and 100 Å in diameter. The Attagel® 50 has a wide range of particle sizes,and only about 65% of the powder is below 2000 Å in length. Both of these particles suspend in polar solvents and may be separated into submicron fluid particle gels in the manner described above with Alon®. Tests were made to incorporate these needle-shaped particles in lieu of Alon® in composition No. 130 and others in System 1. The particles were found to be compatible and to form clear films. In the case of the aluminum hydroxide needles, the films remained soft at 100°C, but at 140°C the hardness greatly exceeded that of the equivalent coatings with Alon®.

The coatings prepared with Attagel® 50, however, became hard at 100°C in the same manner as other films in System 1 with Alon®. In both cases, coatings with needle-shaped crystals were superior to the coatings with the irregularly or approximately spherically shaped Alon® particles, in that crazing after prolonged heating did not occur, and in general the films were stronger and harder.

As the work under this contract proceeded, it became evident that the nature of the polymeric matrix was as important as the nature of the particles embedded in the matrix. A hard particle in a soft matrix or in a water-permeable matrix did not produce a coating having the desired weathering properties; a soft polymeric matrix did not hold the particles firmly, and this composite did not resist abrasion. The System 1, 2, 3, 4 designation was adapted as a classification procedure to enable various composites to be studied by varying the proportion but not the composition of the components.

Silica and SiO_2 refer to the same material, but when making stoichiometric calculations, the chemical formula SiO_2 is used rather than the word silica. In other places "silica" is preferred and used.

The System 1 compositions were clear and free from crazing when subjected to the temperatures and times utilized during the first part of this contract; that is, times generally not exceeding 2 hours. When the time was increased to 6 hours and more, considerable shrinkage occurred in the system and microscopic crazing occurred between the Alon particles which were spherical. No crazing was observed with these compositions, utilizing the submicron rod-like Attagel® 50 particles instead of Alon. Recommendations were that further work be done using the Attagel® 50 rather than the Alon particles at 100°C from 2 to 40 hours.

HARDNESS VS. TEMPERATURE/TIME

Figures 19 through 21 summarize the results of hardness tests versus temperature/time on composition silica/polyvinyl alcohol 70/30, No. 129c. Coated substrates were heated at temperature T °C for t hours, and observations were made of Moh hardness, clarity, crazing, adhesion, etc. The softening or distortion point of the polymer substrate imposed an upper temperature limit. The maximum hardness was reached at an upper safe temperature limit with increased time. Figure 19 shows Moh hardness vs. time at constant temperature (140°C). Most work was performed on Moh hardness vs. temperature/time for times 0 to 20 hours and temperatures 20° to 200°C. When heated for 2 hours, coatings of No. 129c showed a Moh hardness of 5.0 at 100°C and 5.7 at 200°C. However, sheets of Plex II and 55 deform when exposed to temperatures greater than 100°C for many hours. To avoid deformation of acrylic plastics, the maximum temperature is 100°C.

Later in the program, an unexpected and remarkable discovery was made during an investigation of the effect of longer heating time of No. 129c coatings on glass and Plexiglas at 80° to 100°C. This discovery enables substantially harder coatings (> 6) to be produced by heating at moderate temperatures for long periods of time. A heating time of 2 hours is not sufficient to produce maximum hardness.

Figure 21 shows the Moh hardness vs. time in hours at 100°C of No. 129c (silica/polyvinyl alcohol 70/30) coated onto substrate FA5 on 1/8"-thick Plex 55. Specimens employed were the 2-5/8" squares corresponding to the coated plastic panels. The hardness increased to 4.9 at 1 hour, increased to 5.1 at 2 hours, and gradually increased to 5.5

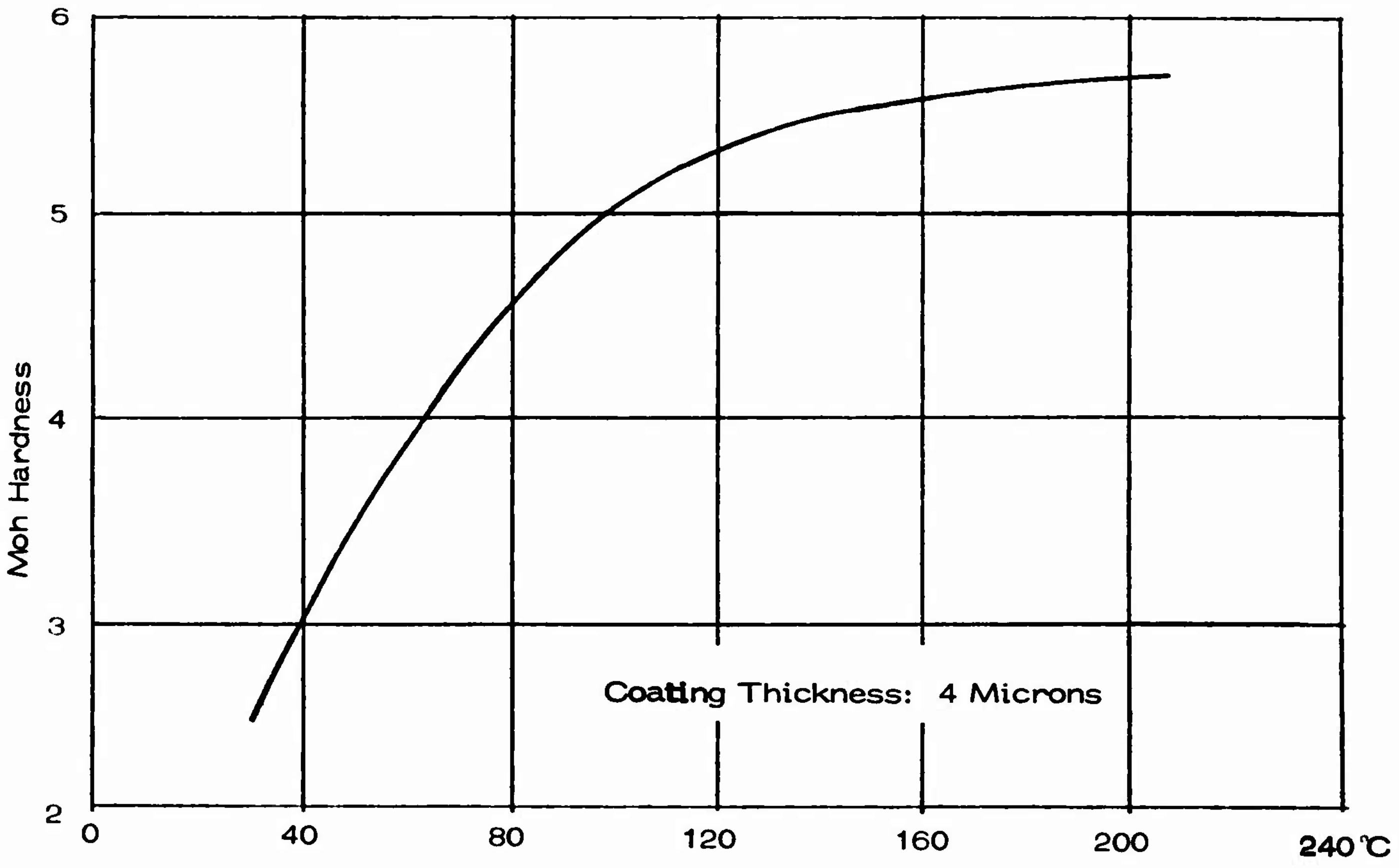


Figure 19. Moh Hardness vs. Temperature in °C With Constant Heating Time of 2 Hours for Constant Silica/pva (70/30).

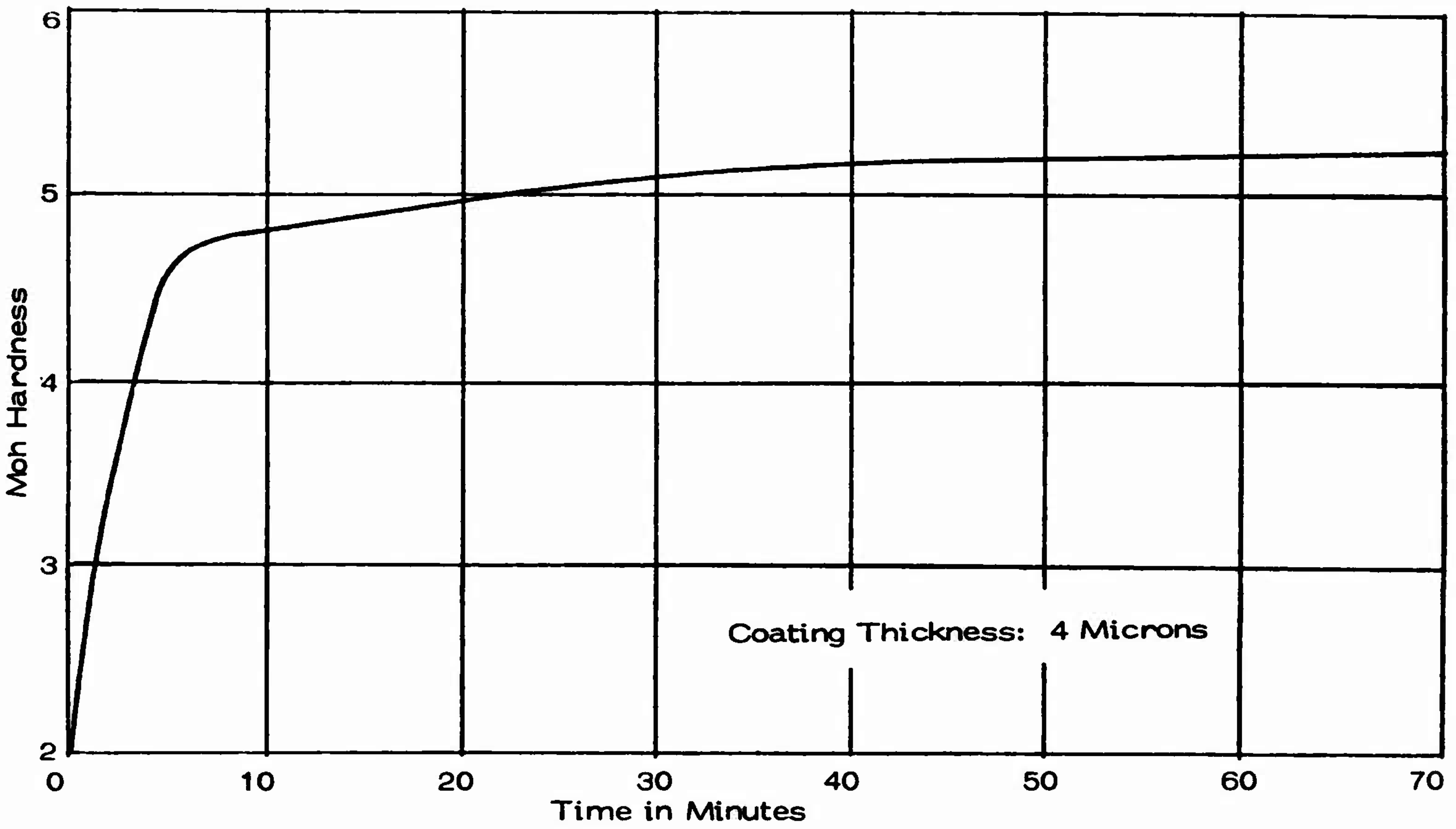


Figure 20. Moh Hardness vs. Heating Time in Minutes at Constant Temperature of 140°C for Constant Silica/pva (70/30).

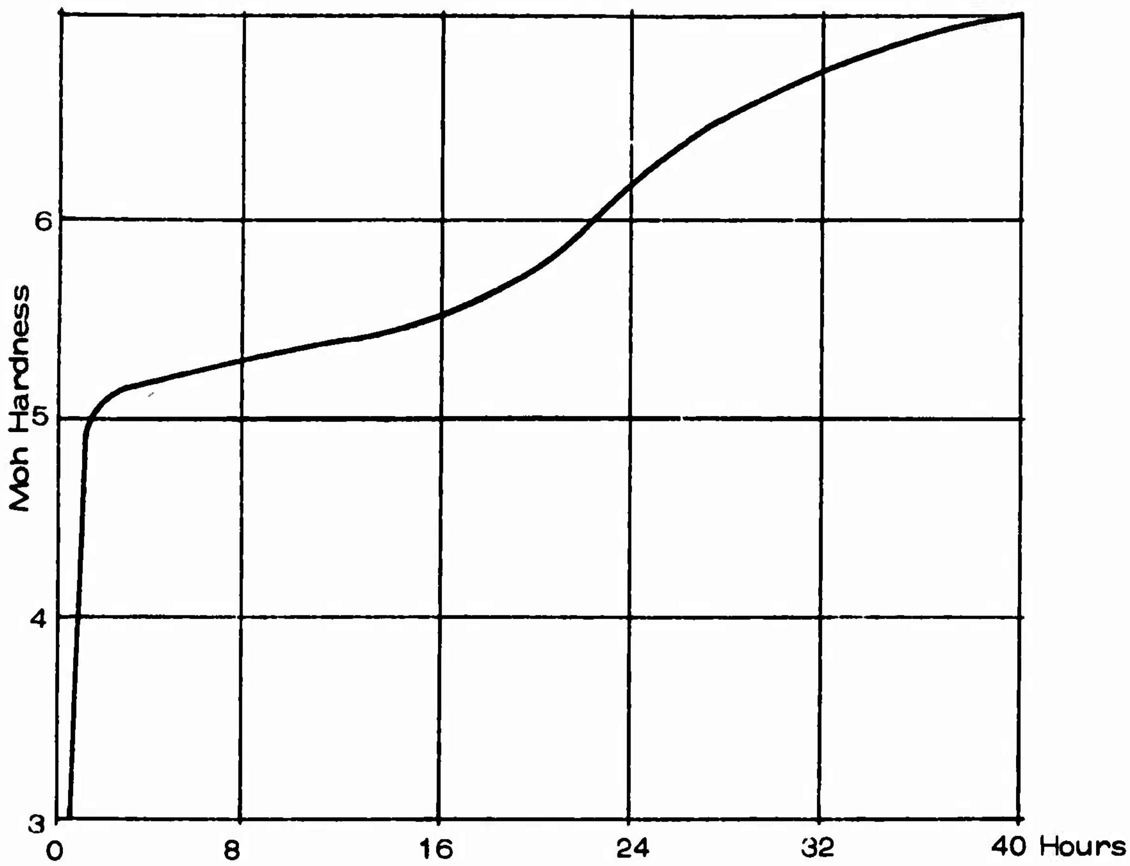


Figure 21. Moh Hardness vs. Heating Time in Hours at Constant Temperature for Constant Silica/pva (70/30) on Plex 55 Coated With Primer FA5 at 100°C; Coating Thickness 4 Microns ±1.

at 16 hours. Thereafter, the hardening accelerated, as indicated by a sudden increase in the slope of the curve. The hardness increased to 6 at 22 hours and to about 7 at 40 hours.

Thick coatings (> 6 microns) are first heated for 4 hours at 70°C to eliminate traces of acid catalyst (HCl) and then are hardened by heating for 24 hours at 95° to 100°C. The improved properties obtained with increased heating time may be explained by increased dehydration and crystallite growth.

Subsequently, compositions shown on the line EF of the triangle chart of Figure 10 were again prepared and tested for longer time periods, resulting in a Moh hardness exceeding 6.5, increased strength, and decreased water permeability.

HARDNESS VS. FILM THICKNESS

The preferred method for increasing the thickness of the coating is to apply a thicker coating utilizing a fluid of greater viscosity and spin coating at about 700 rpm. Viscosity is varied by changing the proportion of solvent, usually water. When more water is added, the viscosity of the fluid decreases. When water is removed, for example, by vacuum distillation, the viscosity increases. Viscosity increases with time as the solids contained continue to polymerize and cross-link. In time, as cross-linking continues, the fluid gels.

Figure 22 shows rpm and Moh hardness vs. film weight per unit area and coating thickness for constant spin time with composition No. 129c.

Figure 23 shows coating thickness vs. spin time at a constant rpm for the same coating weight per unit area. The constant rpm employed in Figure 23 was 3,000 rpm. The size of articles coated on both Figures 22 and 23 was 2-5/8" square. We recommend that this test be repeated at 700 rpm.

Coatings of composition No. 129c (silica/pva 70/30) were applied by spin coating, from 300 to 4,000 rpm, at a constant time of 13 seconds. A speed of 700 rpm for 13 seconds produced a uniform coating of 6 microns thickness. Coatings made at 1,300 rpm or more were less than 3 microns thick, which was too thin and fragile. Coatings made at less than 500 rpm were nonuniform and some were colored.

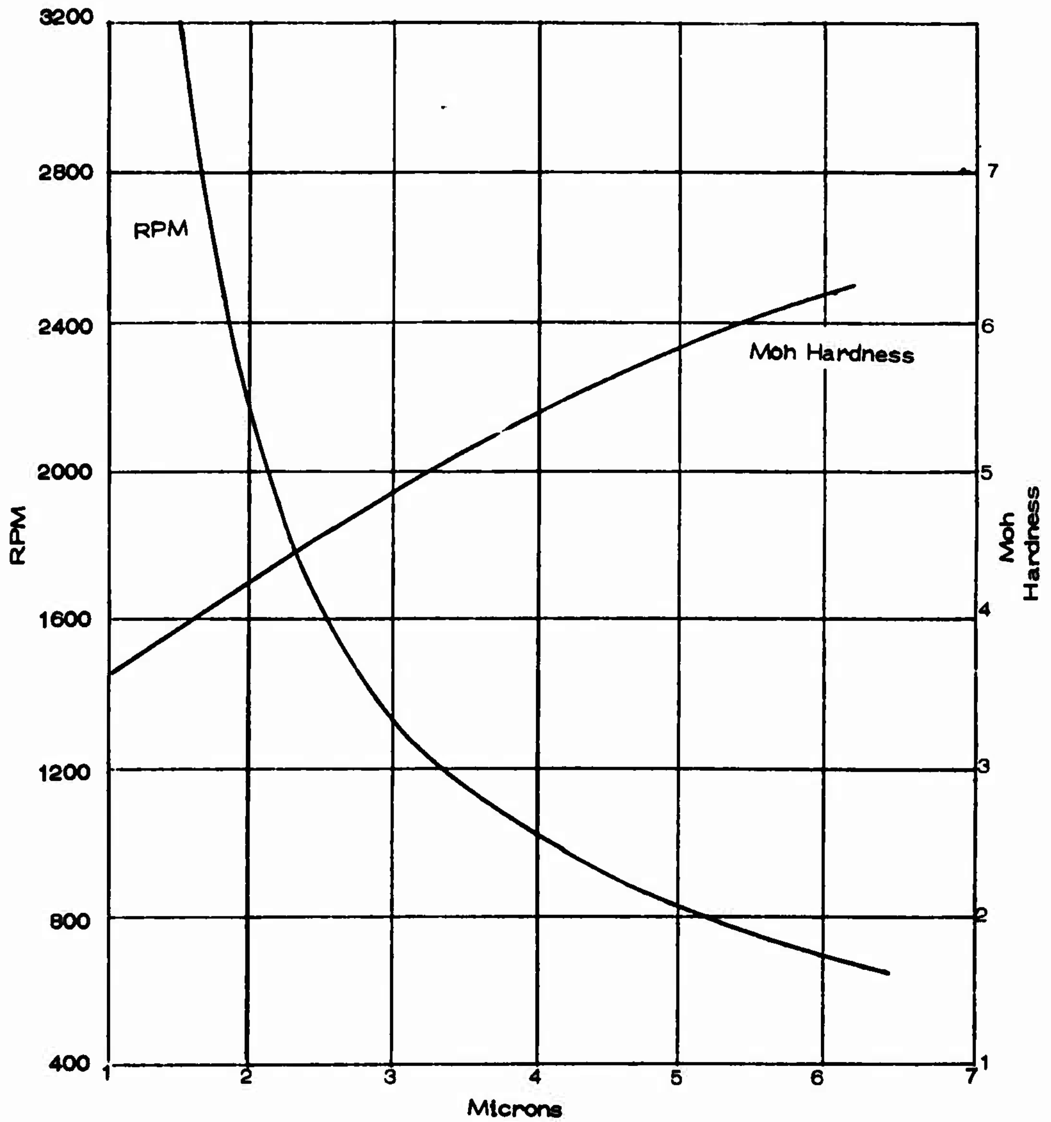


Figure 22. Coatings Applied by Spin Process: Thickness of Coating in Microns vs. RPM for Constant Time of 13 Seconds Using Composition No. 129c.

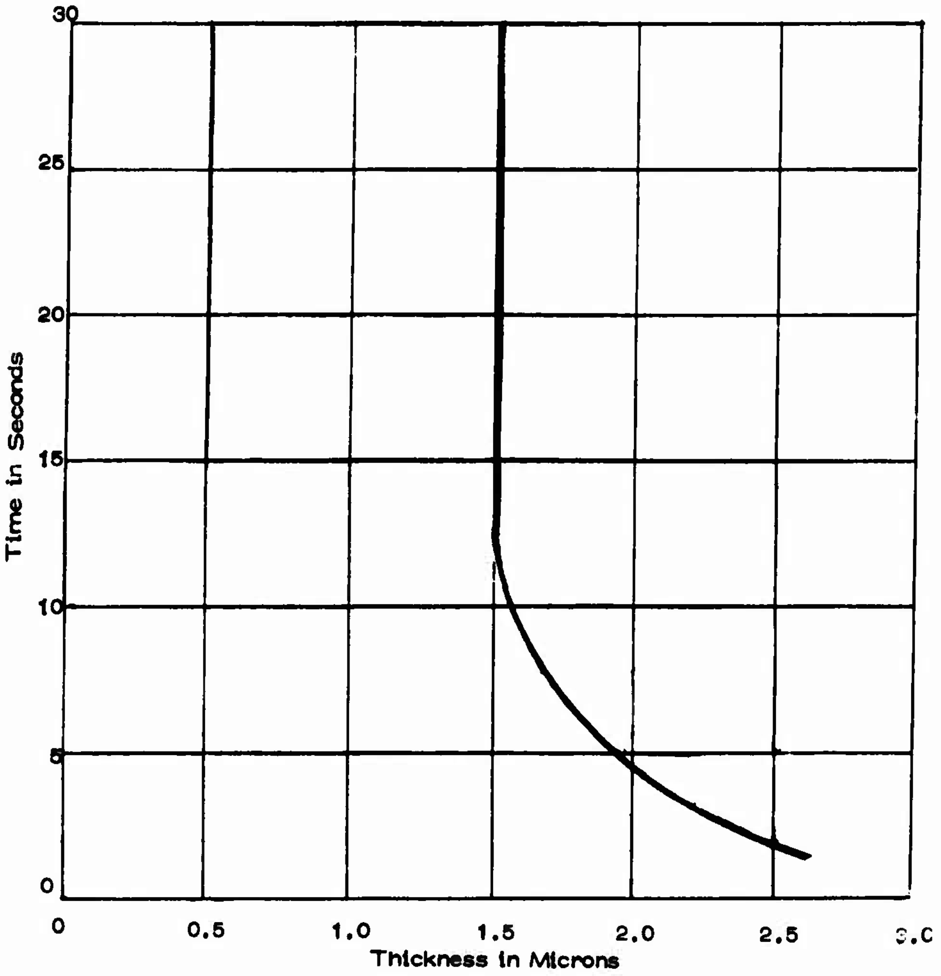


Figure 23. Coatings Applied by Spin Process: Thickness of Coating in Microns vs. Time in Seconds at Constant RPM Using Composition No. 129c at 3000 RPM.

THICKNESS VS. RPM

In early tests, the coating was applied at a speed of 1,800 rpm, for which the thickness was 2.3 microns. By decreasing the speed to 700 rpm, the thickness was increased to 6 microns.

COLOR VS. FILM THICKNESS AND TEMPERATURE/TIME

Coatings thicker than 5 microns which were immediately heated to 100°C for 3 hours became brown-green in color. Coatings of 2.3 microns thickness heated to 100°C for 40 hours were not colored at all. Two layers of 2.3 microns thickness (a total thickness of 4.6 microns), each heated for 40 hours at 100°C, showed no color. Evidently, thicker coatings (> 5 microns) heated immediately after application at temperatures greater than 95°C entrap a component, probably traces of HCl, which catalyzes a dehydration reaction (see Table 6, reactions 3 and 4), forming unsaturated carbon chains known as polyenes, which have a brown-green color. These reactions do not occur in thin layers (< 4 microns), which permit the HCl to escape, or at temperatures below 70°C. Compounds III and VI are polyvinyl silicate; VII and VIII and IX and X show polyvinyl alcohol converted to a polyene in the presence of heat and HCl.

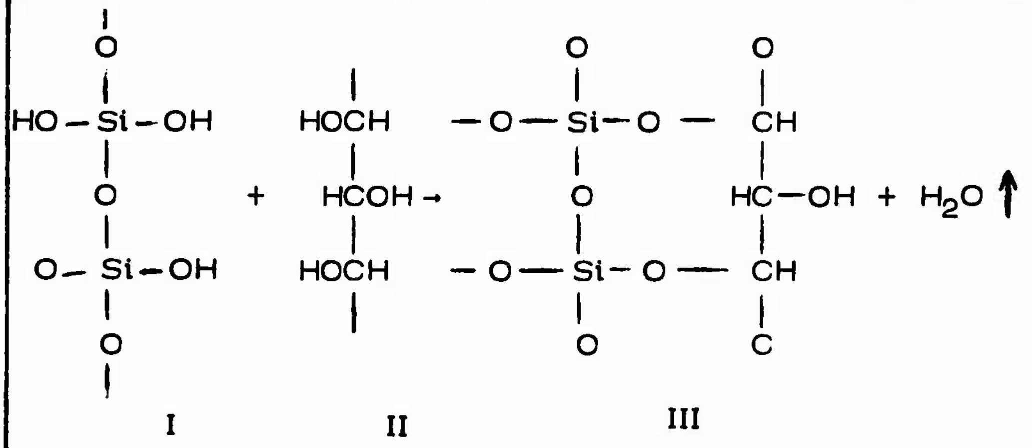
IMPACT RESISTANCE VS. FILM THICKNESS

Coating at 1,800 rpm for 13 seconds provided a layer thickness of 2.3 microns. This coating, when placed over a soft substrate, such as ordinary plastics, was too thin to resist substantial pressure or impact. However, when this coating was placed on glass, it resisted cracking or crazing due to impact or pressure.

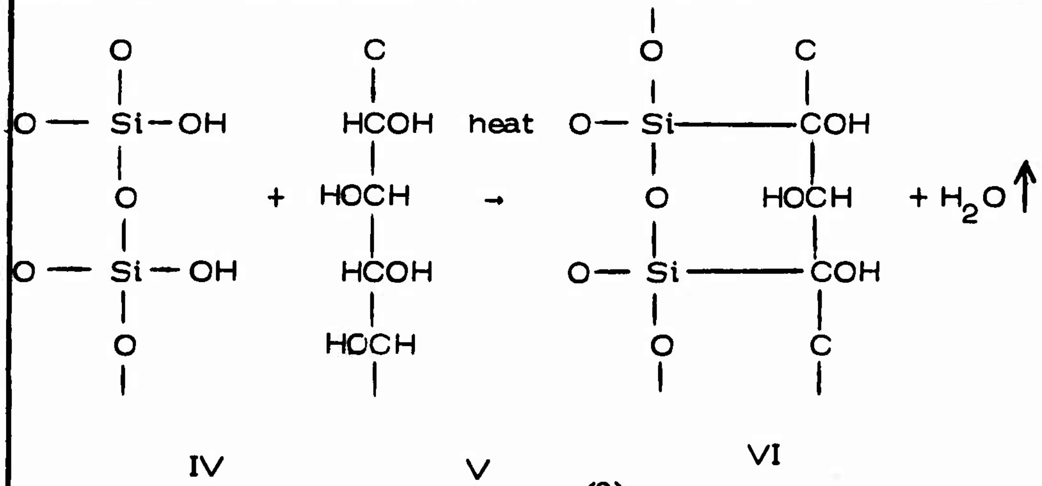
The situation is analogous to a skater on a layer of ice. If the layer is very thin, the skater can break through the layer. However, if the layer is of sufficient thickness, it will support the weight of many skaters and a considerable load can be supported without breaking the layer. The same applies to impact: the thin layer will shatter upon impact, while the thicker layer will resist impact. The coating thickness was increased until loading and impact characteristics were satisfactory. A thickness of 4 to 6 microns was satisfactory.

Referring to Figure 22, the Moh hardness of the coating increases with its thickness, because thicker films have a greater resistance to fracture under pressure, and a greater resistance to scratching. The Moh hardness increased from 4 at 1.5 microns to 6 at 5.5 microns.

TABLE 6. DEHYDRATION REACTIONS

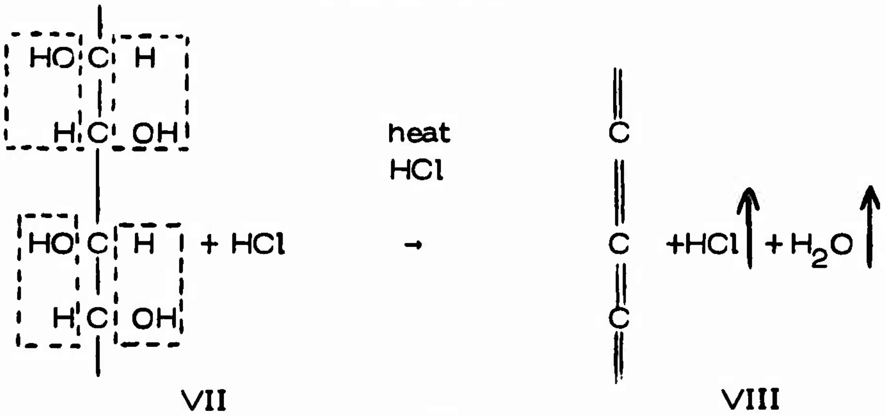


(1)



(2)

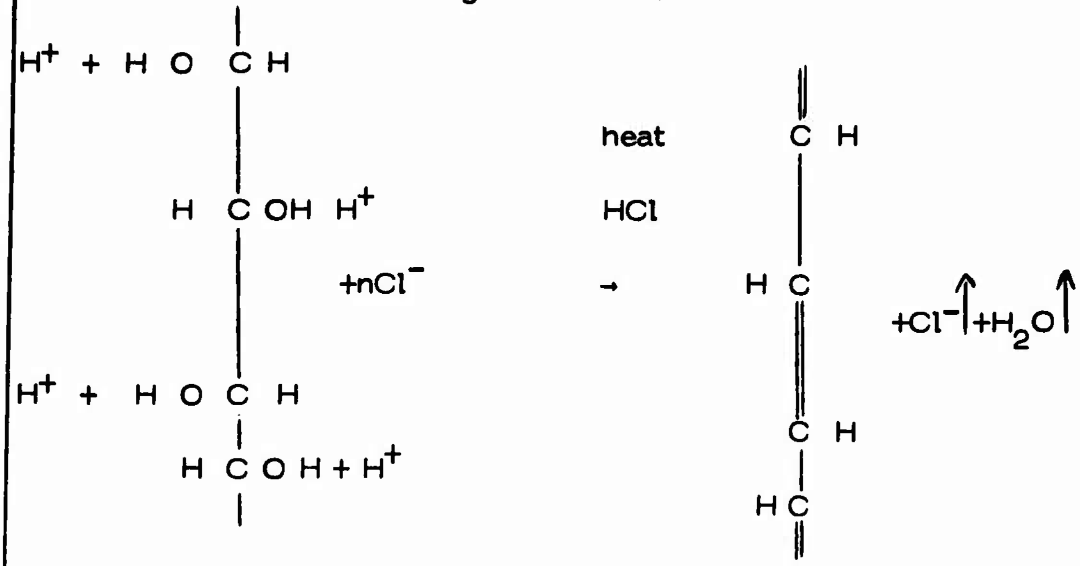
Double Bonds



(3)

TABLE 6. Continued

Single and Double Bonds



IX

X

(4)

MULTIPLE COATINGS

To obtain a thicker coating without coloration, a single No. 129c coating of about 2.3 microns thickness was applied at 1,800 rpm, heated to 70°C for 4 hours, then coated with another No. 129c coating at the same speed and heated to 95° to 100°C for 24 hours, which resulted in a hardness of about 6 without color. However, the second coating must be applied over the first within about 15 minutes after a room-temperature partial drying, before curing and cross-linking of the first coating occurs. If this is not done, the second coating shows poor adhesion to the first coating. Hence, it is preferred to obtain thicker coatings by slower speeds (700 rpm) and a time of about 15 seconds, with a single coating.

PRIMER COATING

System 1 coatings Nos. 119 and 129c showed poor adhesion to acrylic plastics such as Plexiglas G. Primers were investigated to provide a bond. From previous experience, we selected as a primer coat for acrylic plastics, polyvinyl formal (hydroxyl content 7%) Formvar 7/95E. The intrinsic adhesion obtained was due to chemical bonds formed between the System 1 coating, the primer, and the substrate.

A primer coating was developed which shows excellent adhesion to various substrate sheets such as acrylic and polycarbonate, and System 1 coatings are strongly adherent to the primer.

PRIMER COATINGS

	Parts by Weight	
	FA5 (acrylic)	FA6 (polycarbonate)
polyvinyl formal 7/95	5	5
acetic acid	95	92
DAA	-	3
	100	100

This primer was applied to the substrate sheet by spinning at 1,800 rpm. It formed a thin, transparent coating. This was heated for 2 hours at 90°C. After cooling the substrate to 20°C, a System 1 composition was then coated by spinning onto the primer and heated for a given time and temperature. No splitting away of the coating was obtained if the coated plastic sheet was broken, and the coating could not be removed by abrasion or lifted away with adhesive tape.

EVALUATION

Solvents

Composition No. 129c was coated on glass, heated to 120°C, and dipped into the solvents listed in Table 7 for 20 minutes at 25°C.

TABLE 7. EFFECT OF SOLVENTS ON COMPOSITION NO. 129c 70/30, SILICA/PVA

Solvent		Effect
Acetone		NONE
Methyl Alcohol		NONE
Methyl Amyl Ketone		NONE
Toluene		NONE
Xylene		NONE
Water	25°C	NONE
Water	90°C	NONE

When coating plastic substrates, solvent evaluations were made with coating No. 129c, heated for 2 hours at 100°C. Since the plastic substrates may be affected by the solvent, in these cases the solvent was applied only to the outer surface of the coating using a sponge in contact with the coating. In all of these cases, the results were the same as given in Table 7.

Other compositions reported were not tested because both Alon and silica are insoluble in all of the solvents noted in Table 7, and in most cases, the matrix is of the same general composition as coating No. 129c.

Boiling Water

A No. 129c coating was placed onto Plexiglas which had been subcoated with Composition FA5. It was immersed in boiling water for 5 minutes. The coating was not affected. It remained clear and adhered to the Plexiglas. However, the coating was softened due to water penetration and absorption.

Humidity

Silica/Alon compositions, after remaining 2 days in a humid atmosphere, showed decreased hardness. By comparison, on exposure to moisture, the hardness of compositions of pva/silica (129c) or pva/silica/Alon (119) did not change. The presence of only 5% polyvinyl alcohol in silica/Alon compositions was sufficient to avoid the decrease in hardness. These compositions form clear coatings exceptionally insoluble in water, probably due to the formation of the compound pva-silicate.

The humidity tests were performed on various System 1 coatings, including No. 129c. Coatings on amorphous substrates such as glass or Plexiglas did not change. However, when these coatings were placed over a crystalline structure such as a stretch-oriented polymer, then epitaxial crystallization,evidenced by parallel line crazing, was observed. Epitaxial crazing does not occur when utilizing amorphous substrates such as glass or Plexiglas. However, it is expected that epitaxial crystallization will not occur when utilizing rod-like (attagel) rather than sphere-like (Alon) particles.

Flexibility

All the films tested showed excellent flexibility when applied to a plastic surface, such as thin polymethyl methacrylate (Plexiglas). The films could be bent repeatedly through a radius of about 1 cm without cracking or flaking. However, the adhesion to Plexiglas was poor. Compositions from 0/100 to 25/75 pva/silica crystallized and crazed into parallel lines when coated onto a crystalline substrate and flexed. The crystallization always occurred in lines parallel to the crystal axis of the crystal substrate. This indicates epitaxial crystallization or induced crystallization, in which the crystal axes of the silica or polyvinyl silicate become parallel to the crystal axis of the substrate. At more than 40% polyvinyl alcohol, no epitaxial crazing was observed. Composition No. 129c, which comprises 30/70 pva/silica, withstands bending and does not normally craze. However, when No. 129c was exposed to 100% relative humidity at 38°C for 3 days on a crystalline substrate, then epitaxial crystallization occurred. Additives will be sought to keep the structure amorphous. Cymel (No. 153) shows promise; see Tables 5 and 8.

Ultraviolet Light Exposure

Panels of Plexiglas 55 3/16" thick were subcoated with Primer FA5, and then the No. 129c top coat was applied. They were heated to approximately 100°C for 2 hours and then exposed to ultraviolet light for 30, 60, and 90 minutes. The exposure was 4½" below a Sperti sun lamp, 100 volts, 425 watts. The panels were rotated on a turntable under the ultraviolet lamp, exposing them approximately half the time to the ultraviolet. This was to avoid excessive heating during the ultraviolet exposure. The coating remained clear and free from crazing. Increased exposure time to ultraviolet appeared to slightly increase the hardness, by about ¼ Moh. The initial hardness was estimated to be 4.9, since when using the eraser test, barely perceptible scratching was observed when viewed in a strong light against a dark background. After exposure to ultraviolet light for about 90 minutes and repeating the eraser test, there was no visible scratching. However, the hardness was somewhat less than 5.5, since steel wool produced some scratching; therefore, the ¼ Moh designation was used because the hardness measured between 5 and 5.5, which is 5.25 Moh (see Table 1). The increased hardness was possibly due to the ultraviolet. There appeared to be no degradation of the film, but possibly a slight increase in the hardness on long exposure to ultraviolet light.

TEST PROCEDURE ON SUPERHARD TRANSPARENT COATINGS

OPTICAL MEASUREMENTS

Light Transmission

A Perkin-Elmer Spectrophotometer was used to measure transmittance vs. wavelength with substrate only and substrate with coating. There was no apparent difference in light transmission for substrate and substrate with coating.

Haze

The sample coating was visually examined in strong sunlight or equivalent against a black background. Haze comparison (greater than, less than) was made against a Plexiglas II and a polycarbonate panel. There was no perceptible difference in haze.

PHYSICAL MEASUREMENTS

Flexure

The coating was placed on a flexible substrate (an acrylic plastic having a thickness of 1 mm) and bent through a 25 mm radius for 10 cycles. There was no crazing or separation.

The flexure test is similar to ASTM Standard D1010 for a protective coating on metal. To avoid fracturing the plastic substrate, it was necessary to modify this test to increase the bending radius from 12.7 mm to 25 mm, to decrease the bend angle from 180° to 90°, and to place the coating on a 1-mm-thick plastic.

Impact

The coating was placed on a 1/8" (3 mm) thick Plexiglas II sample and impacted by an approximately 200-gram steel ball falling from a height of 50 cm. There was no apparent fracture of the coating from the substrate.

The impact test used was similar to ASTM G14, which was devised for a plastic coating on metal pipe. Experience with plastic lenses in the sunglass industry suggested that the ball weight be decreased to 200 gm and the height to 50 cm.

Hardness and Abrasion Resistance

For a given Moh hardness,[1] rubbing of an abrasive on a material at any pressure or number of cycles will not produce visible scratching if the Moh hardness of the material exceeds the Moh hardness of the abrasive. The criterion is the presence or absence of scratches. Tests such as the eraser test shown in column D of Table 3 are useful for measuring hardness and abrasion resistance only for soft coatings (< 5). These tests were not useful for measuring the Moh hardness of superhard coatings

(> 5). For a hardness of 5.5, the hardness test used was steel wool attached to the end of a pencil. For hardnesses of 6, a sharp-pointed glass scriber was attached to the end of the pencil. For hardnesses of 7, a quartz crystal was attached to the end of the pencil. The Moh hardness results obtained by these tests are given in the figures; for example, Figure 9. Various materials listed on the Moh scale were reduced to powder and used to calibrate Moh hardness tests. The Moh hardness test shown in column C of Table 3 was used for superhard coatings based upon the accepted Moh hardness of materials listed in columns A and B. The materials shown in column C are materials used as a Moh hardness comparison in this work. The eraser test shown in column D is performed with ten strokes at 300 grams pressure on a pencil eraser. The resulting mark is observed in a strong light against a dark background.

Adhesion

Adhesion was determined by applying a strip of cellulose adhesive tape to a scribed coated plastic and removing the tape by a snapping pull at 90° to the substrate. There was no separation of the film from the substrate in the chosen primer and coating compositions.

Solvent Resistance

The coated transparent plastic was subjected to 20 minutes of exposure to the following solvents: methyl ethyl ketone, acetone, methyl isobutyl ketone, toluene, hexane, butyl alcohol, methyl alcohol, lacquer thinner, isopropyl alcohol, and xylene. These solvents did not decrease the optical and physical properties of the coated transparency. Coating No. 129c was the only coating tested, since Alon and silica are insoluble in all of the above-listed solvents.

WEATHERING

Humidity

The coated substrates were exposed to water-saturated air at 45°C for 24 hours. After humidity exposure, the panels were examined for hardness, peeling, crazing, etc. It was intended to repeat the entire group of tests after humidity exposure, but this could not be done because of time and manpower limitations. Consequently, these tests were not repeated.

Ultraviolet Rays

Test samples were exposed to an S-1 ultraviolet bulb for 24 hours on a revolving table. No change was noted in the appearance of the coating as to crazing, haze or other apparent defects.

Temperature

Samples were held continuously for 24 hours at 80°C. Hardness was measured, as described. Hardness increased. Water resistance increased. The coating remained clear and free from haze.

RESULTS

SUBMICRON FLUID SUSPENSIONS

Tests were started with Alon. Alon comprises aggregates of 100 Å submicron irregular particles of fumed aluminum oxide. Most of the aggregates were separated in the disperser into the 100 Å particles suspended in a fluid. These 100 Å particles were then centrifugally separated from the larger aggregates. Alon forms an excellent suspension in distilled water. The aggregates were initially separated by dispersing the water-Alon suspension in a "Polytron" Disperser at 18,000 rpm for 1 hour. An "on-off" cycle timer prevented overheating. This suspension was then centrifuged at successively higher rpm's in 1,000-rpm increments up to 9,000 rpm, the limiting speed of our centrifuge. The sediment at the bottom of the centrifuge tubes was milky in the lower speed ranges; in the higher speed ranges from 6,000 to 7,000 and from 7,000 to 8,000, the sediment was decreasingly translucent; while between 8,000 and 9,000 rpm, the sediment was a clear gel.

Due to the abrasive action of the Alon, the bearing in the "Polytron" Disperser became worn in about 1 hour and had to be replaced, which was a time-consuming and costly procedure. To overcome this difficulty, another type of disperser was tested: a Gaulin Submicron Disperser. This utilizes a jet of the suspension propelled against a tungsten carbide plate at a pressure up to 10,000 psi. The plate wore slowly and was replaced only after 50 hours time. The test of this device was successful and we obtained this device for our work.

Clear gels were made by homogenizing at 18,000 rpm for 1 hour with the "Polytron" Disperser, or by using the Gaulin Disperser at 8,000 to 10,000 psi and circulating the suspension several times. This clear gel was readily dispersed in water, ethanol and other polar solvents.

This result is a striking confirmation of the premise upon which this project is based, particularly because of the substantial difference in the indices of refraction between aluminum oxide and water; that is, (1.76 - 1.33) = 0.43. The indices of refraction for the crystalline form of aluminum oxide versus the liquid form of water were given. Submicron aluminum oxide and water form a clear gel. Hence, submicron particles do not scatter light despite substantial difference in the indices of refraction between the particles and the medium in which they are dispersed.

SUBMICRON PARTICLE/FLUID GELS

Aluminum oxide has a strong positive charge and is suspended only in strong polar solvents. Many plastic compositions are not soluble in water, but are dissolved by polar solvents which disperse and suspend the submicron aluminum oxide particles. Alon suspensions were made in polar fluids such as water, n-propanol, n-methyl-1-pyrrolidone, dimethyl formamide, and phosphoramide. Clear gels were formed with these fluids when the homogenized suspension was sedimented by centrifuge in the slot between 8,000 and 9,000 rpm. When the supernatant fluid was poured off, a clear gel remained. With water, the clear gel contained 45% aluminum oxide. The aluminum oxide concentration of the gel was determined by weighing a sample of the gel. The gel was heated at 100°C to evaporate the water. The residue was weighed and divided by the initial weight of the gel to obtain the concentration of aluminum oxide in the gel, which was determined to be 45%.

In a similar way, other submicron particles formed clear transparent gels. For example, water and silica, magnesium aluminum silicate needles (Attagel), and aluminum hydroxide (Baymal).

POLYSILICIC ACID

The polysilicic acid solution used in these formulations was prepared by shaking tetraethyl orthosilicate with water. For the reaction to occur, the water must contain about 1% hydrochloric acid as a catalyst. The tetraethyl orthosilicate and water react stoichiometrically to form 21.4% SiO_2 solids dissolved in ethyl alcohol which condenses to a siloxane polymer containing hydroxyl groups useful in cross-linking reactions. The reaction and molecular weights are given:

$$4H_2O + (C_2H_5)_4\ SiO_4 \xrightarrow{\text{HCl}} 4C_2H_5OH + H_4SiO_4$$

$$72 + 208.1 \rightarrow 184 + 96.1$$

$$\underline{280.1 \qquad\qquad\qquad\qquad 280.1}$$

$$n(H_4SiO_4) \xrightarrow{\text{heat}} (SiO_2)_n + n.(2H_2O)$$

$$\underline{96.1 \rightarrow 60.1 + 36}$$

Problems were encountered in the preparation of a polysilicic acid solution suitable for use in these compositions. Early efforts resulted in solutions having a pot life of 2 hours, and these sometimes gelled before use.

Ethyl alcohol is not compatible with polyvinyl alcohol, resulting in cloudy coatings. The proportion of polysilicic acid with the polyvinyl alcohol was limited because the polysilicic acid was dissolved in ethyl alcohol, which produced cloudy coatings.

Various percentages of HCl were tested as catalysts. At 0% the reaction occurs slowly or not at all. At 2% or more, the reaction proceeds too rapidly and may cause gelling, showing that too many polysilicate bonds have been utilized. An optimum appears to be 1%.

Methods for the Preparation of a Polysilicate/Alon Suspension

1. Tetraethyl orthosilicate (TEOS) 85 parts and water 15 parts with 1% HCl are mixed and shaken, producing partially hydrolyzed polysilicic acid, unreacted TEOS, and Ethanol. The unreacted TEOS subsequently is fully reacted in the formulation of the composition.

2. The 45% Alon/water paste is added in the required proportion of Alon/silica. (For example, in No. 119, a ratio of 20/75, there are 5 parts of polyvinyl alcohol.) This is mixed, shaken, cooled and heated at 60°C for 1 hour and then cooled to 25°C. A clear suspension fluid comprising Alon in polysilicic acid solution is formed. The submicron aluminum oxide particles are dispersed most uniformly in the polysilicic acid and may be used in coatings of silica/pva/Alon of excellent clarity and hardness. The pot life is about 1 day.

3. The addition of 35 parts water to 100 parts of the suspension produced by method (1) and subsequent evaporation of 35 parts of fluid removes about 35 parts of the ethyl alcohol and substitutes 35 parts of water, leaving polysilicic acid solution in water/ethanol ~ 50/50. This is compatible with Alon and/or polyvinyl alcohol in any proportion.

Method (3) gives a thicker coating but has a shorter pot life. Otherwise, coatings produced from polysilicic acid made by methods (2) and (3) are equivalent. Method (3) was employed in the optimum compositions.

Compositions

Clear films were produced when the clear Alon gel was mixed with a polymer soluble in polar solvents.

Alon-n-propanol gel is compatible with alcohol soluble resin systems such as polysilicic acid, silicon polymers such as monomethyl polysiloxane resin, and organic polymers such as polyvinyl acetate alcohol copolymer.

Alon/water gel and polyvinyl alcohol form a clear hard film. Various proportions of the Alon/water gel with 10% polyvinyl alcohol dissolved in water were used. Clear smooth films were obtained up to 70% Alon, 30% polyvinyl alcohol. Above 70% Alon, the films became hazy.

Polyvinyl alcohol and polysilicic acid solutions in water, upon drying and heating, form a clear hard coating, insoluble in water and other solvents. This coating is strongly adherent to glass substrates, but has poor adhesion to acrylics; however, adhesion can be obtained with a primer coating.

The three components of System 1 (polysilicic acid (silica)/polyvinyl alcohol/aluminum oxide (Alon) submicron hard particles) are water-soluble or dispersible, are compatible in all proportions, and have hydroxyl groups which form chemical bonds with the elimination of water. In most proportions, a water-insoluble transparent coating is formed. Hardness varies with the composition. Many compositions in this system were prepared in various proportions and were coated onto various substrates, and their properties were studied.

Various materials were tested for compatibility and cross-linkage with the components of System 1 compositions. The results, shown in Table 8, illustrate the many possibilities.

TABLE 8. COMPATIBILITY OF MATERIALS WITH SYSTEM 1 COMPOSITIONS

Material	Compatibility
Polyvinyl Pyrollidone	none
Aluminum Monophosphate	none
Hexamethoxymethylmelamine (Cymel®)	excellent
Methacrylic Acid	excellent
Diacetone Acrylamide (DAA)	excellent
Organic Titanates	slight

The objective was to obtain materials compatible with System 1, which were non-water-absorbant when fully cross-linked. The purpose of Table 8 is to show certain materials compatible with System 1 compositions; that is, those materials which will mix and form a clear fluid and a clear solid upon evaporation. The materials listed form cross-links with the hydroxyl groups of System 1 components.

STRETCHED PLEX

Formula No. 129c was coated onto stretched Plex. When this was heated to about 100°C, substantial shrinkage occurred, with the greatest shrinkage occurring on the coated side of the sheet.

The coatings in which shrinkage had occurred were harder, tougher, and less water-pervious than coatings placed on other surfaces which did not shrink. These improved properties may be attributed to the lateral, as well as thickness, shrinkage.

OPTIMUM COMPOSITIONS IN SYSTEM 1

Data was obtained for 15% and 20% constant pva. The best composition (No. 131A) was silica/pva/Alon 62.5/20/17.5, which had a hardness of 6. This data is plotted in Figures 15 and 17, which show that superhard (Moh > 5) coatings are produced for constant 20% pva from 11% to 23% Alon with a remarkably sharp peak of about 6.5 at 15% Alon. After 2 hours at 100°C, compositions 119, 120, and 130 were about ½ Moh harder, and were thus recommended over 131A.

One of the optimum compositions of silica/pva (70/30) was No. 129c. This is shown by an X-ray spectrogram of this silica/pva composition, which was obtained to determine the presence of crystallites. This composition was coated on Mylar, dried, and stripped away. It was found that with reference to the side-angle X-ray pattern of the silica coating material, the halo at 3.8 Å. Such a structure is typical of vitreous silica, which recent theories regard as very small crystals rather than amorphous structures. The particle size might well be larger than the crystallite size, but it is definitely not comparable to the wavelength of light.

Another optimum composition, No. 120, comprises Alon and polysilicate which was dehydrated and cross-linked to itself and to the particle. Optimum compositions Nos. 119 and 130 contain all three components in System 1, while Nos. 120 and 129c contain only the best of two components;

however, both appear to contain submicron silica crystallites embedded in an amorphous polymeric matrix. All the optimum compositions contain cross-linked Alon, polysilicate and polyvinyl alcohol in the proportions listed in Table 9, except No. 129c, which contains no Alon.

TABLE 9. % SOLIDS BY WEIGHT OF CANDIDATE OPTIMUM COMPOSITIONS

Number	Alon	Silica	Polyvinyl Alcohol	Hardness A	Hardness B
120	22	78	0	6.5	
119	20	75	5	6.5	
130	15	70	15	6.5	
129c	0	70	30	5.0	7

Key: A = Heated 2 hours @ 100°C
B = Heated 40 hours @ 100°C

Coating thicknesses were approximately 4 microns. The percentage of silica in the polysilicic acid employed is only important with relation to the solvent employed before the coating is hard. When the solvent evaporates, the residual solids ratio of silica/pva/Alon is the determining factor.

With the data available at the end of the contract, composition No. 129c had the greatest hardness and was best understood of all the coatings tested. Compositions Nos. 119, 120, 130 and 131A contained spherically shaped Alon particles. These compositions were not recommended because with increased heating time crazing was observed. Our recommendation is to substitute a submicron needle-like crystal such as magnesium aluminum silicate (Attagel) for Alon. The crazing should be eliminated because of the structural reinforcement of the coatings by the rod-like particles.

CONCLUSIONS

We have confirmed the premise underlying this project; i.e., that submicron transparent particles can be dispersed in high concentration within a polymer film to form a transparent film and that the hardness increases with the percentage of hard particles in the film.

The hardness of the composite increases with the percentage of hard particles until the adhesion of the hard particles to the matrix is decreased by the presence of insufficient matrix to hold the particles. There is a critical particle/matrix ratio for obtaining maximum hardness. The maximum hardness is increased by: (1) utilizing harder particles, (2) a chemical binding of the particle to the matrix, (3) particles having elongated or needle-like shape rather than irregular or spherical shape, and (4) orientation of the long axis of the needles normal to the surface.

Alon is amorphous aluminum oxide, which is not as hard as crystalline aluminum oxide; and this limits the maximum hardness of an Alon/matrix composite coating to about 6.5. The maximum hardness of the Alon appears to be about 7, while the reported hardness of aluminum oxide crystals is 9.5. Hence, a further increase in hardness of the coating should be achieved with crystalline needle particles of aluminum oxide to replace the Alon.

Submicron aluminum hydroxide AlOOH needles were obtained. These formed transparent hard coatings with the optimum compositions. However, the coatings were softer than with Alon at temperatures up to 100°C, and harder than the Alon coatings at temperatures of 140°C or more. However, in many cases this temperature exceeds the softening or shrinkage temperature of the plastic substrate, and this may preclude the use of the aluminum hydroxide needles.

Another submicron crystalline needle is magnesium aluminum silicate $MgAlSiO_3$. Optimum compositions prepared with these submicron needles are similar to the same compositions made with Alon. However, because of the needle shape, these compositions are more resistant to crazing and impact, and are harder. Because no further dehydration is required to obtain the hard crystalline needle, compositions using this material harden in the range of 80° to 100°C, which is useful with most plastic substrates.

The silica/pva matrix formed crystalline silica crystallites in situ. The crystallites, if quartz, would have a hardness of about 7, and this appears to be the reason for the hardness of the composition No. 129c coatings (silica/pva 70/30).

Various cross-linking additives which were tested suggest that bulky molecules such as Cymel, while effective cross-linking agents, produce coatings of somewhat decreased density and hardness.

Cross-linking agents comprising small molecules such as the tetra-functional inorganics, silicates, zirconates, and titanates tend to increase the hardness and show promise for decreasing water penetration.

The hardest films were those which were the most fully dehydrated by prolonged heating. As the dehydration proceeded, shrinkage occurred both normal and parallel to the surface; up to a certain point the shrinkage can be tolerated without cracking the film, but if the maximum dehydration is required to form the hardest film, then the shrinkage must be accompanied by a corresponding shrinkage of the substrate. This may be accomplished in two ways: (1) by an initial stretching of the substrate and a subsequent relaxation in a prepared fixture which bends the substrate into a sphere and allows it to relax to a plane surface; (2) by utilizing a prestretched polymer sheet, permitting controlled shrinkage of the sheet in a plane.

The latter has been observed and confirms this approach, although not under controlled conditions; the former remains for further work.

Other directions have been suggested involving the use of porous coatings which subsequently are filled with a matrix to produce a composite. These coatings have been given the acronym "POPAC".

The work resulted in several coatings which appeared to meet all the specified requirements, but more work must be done to explore in more depth the approaches opened by this work.

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APPENDIX

FORMULATION OF OPTIMUM COMPOSITIONS

In producing the optimum compositions, the following ingredients are used:

Solution "A"	Parts by Weight of Solution
Polyvinyl alcohol 71-30	10
Distilled water	90
Total	100

Solution "B"

Hydrolyzed tetraethyl orthosilicate reacted with water and 1% HCl to form polysilicic acid in ethanol. Water added to form 18.3% as SiO_2.

Solution "C"

A submicron particle suspension of Alon in water containing 43% Alon; particle size of less than 200 Å in 57% water.

Solution "D"

Same as solution "C", but with Attagel submicron needles substituted for the Alon.

TABLE NO. 10 FORMULATION OF OPTIMUM COMPOSITIONS

Materials			
Initial	Final	Solution or Suspension	% Solids
A	Polyvinyl Alcohol	Water	10
B	Polysilicic Acid as SiO_2	Ethanol and Water	18.3
C	Alon	Water	43
#120	A	-	-
	B	425	78
	C	510	22
	% Solids = 10.7%	935	100
#119	A	50	5
	B	410	75
	C	47	20
	% Solids = 19.8%	507	100

TABLE 10 - Continued

Materials		Solution or Suspension	% Solids
Initial	Final		
#130	A	150	15
	B	380	70
	C	350	15
	% Solids = 18.3%	880	100
#129c	A	30	30
	B	370	70
	C	-	-
	% Solids = 25%	400	100

LIST OF SYMBOLS

		Units
d	thickness of plastic sheet	cm
d_o	thickness of coating layer	cm
L_1	length of center line of plastic sheet subtended by angle θ	cm
L_2	length of inner surface of plastic sheet subtended by angle θ	cm
r_1	radius of curved plastic sheet to center line = r	cm
r_2	radius of curved plastic sheet to inner surface	cm
θ	angle subtended by curved plastic sheet	deg