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Charles D. Gagliardi

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Kris A. Berglund
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DEVELOPMENT AND CHARACTERIZATION OF POROUS, OPTICALLY CLEAR, METALORGANIC THIN-FILM COATINGS

By

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ABSTRACT

DEVELOPMENT AND CHARACTERIZATION OF POROUS, OPTICALLY CLEAR, METALORGANIC, THIN-FILM COATINGS

By

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The controlled hydrolysis of group IV 'd' block metal alkoxide carboxylates (metal alkoxoacylates) at room temperature can provide excellent coating materials for applications requiring porous, optically clear, thin-film coatings. This work demonstrates a method for making water soluble films from hafnium isopropoxide acetate complexes, and compares the films and processing behavior associated with titanium, zirconium, and hafnium alkoxide acetates. Raman and IR spectroscopy are used to characterize the materials. A series of titanium isopropoxide carboxylates are also examined to determine the effect of carboxylic acid chain length on film quality. This study shows that the titanium isopropoxide valerate complexes produced stable, organic solvent and water insoluble films. The Raman spectra for the various coating solutions demonstrate their strong chemical similarity and dramatically show the chemical effect of adding water. Slight differences among the spectra of the hydrolyzed solutions may be correlated with differences in film quality.

I dedicate this work to Charles and Leola Gagliardi,

two of the most patient, loving, and generous people I have ever known.

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INTRODUCTION

This work investigates the controlled hydrolysis of titanium, zirconium, and hafnium metal alkoxide carboxylates at room temperature to provide coating materials suitable for applications requiring highly porous, small pore size, optically clear, thin-film coatings. The significance of this research rests on the usefulness and variety of the applications. The films could be used as separation process membranes or as supports for catalysts or photocatalysts. Optically clear catalyst support films could be used to allow vibrational spectroscopy studies of the catalyzed reaction. Due to the ambient processing temperature of these materials, many delicate organic macromolecules could be incorporated into these films which would be destroyed by higher processing temperatures. Thus, these materials could be used to create a variety of optically probed chemical sensors.

The hydrolysis of metal alkoxide carboxylates may be viewed as the sol-gel processing of a metal alkoxide using a carboxylic acid as a chemical modifying agent. However, since the presence of the carboxylic acid creates fundamental changes in the processing characteristics of the precursor and the properties and chemical composition of the product, I have chosen to treat metal alkoxide carboxylates in a category of their own. Nevertheless, since the hydrolysis of metal alkoxide carboxylates is clearly included within the very broad realm of sol-gel chemistry, a brief review of this topic will be given. Metal alkoxide carboxylates, otherwise known as metal alkoxoacylates, share in the chemistry of both metal alkoxides and metal carboxylates; therefore, relevant information concerning both these types of compounds will be reviewed. Similarly, information concerning alcohols, carboxylic acids,and esters will also be presented. The processing of the metal alkoxide carboxylates can lead to materials which are highly soluble in water (produced with acetic acid) or materials which demonstrate insolubility in water and increased resistance to many organic solvents (produced with valeric acid). Because of fundamental differences in the processing methods for soluble and insoluble films, the two topics will be treated separately.

On the topic of water soluble materials, a method for making films from hafnium isopropoxide acetate complexes will be demonstrated, and the films and processing behavior associated with titanium, zirconium, and hafnium alkoxide acetates will be compared. Characterization of the materials will be accomplished with Raman and IR spectroscopy.

The investigation of water insoluble films will involve an examination of a series of titanium isopropoxide carboxylates to determine the effect of carboxylic acid chain length on film quality. This will show that the titanium isopropoxide valerate complexes produced stable, organic solvent resistant and water insoluble films. The Raman spectra for the various coating solutions will demonstrate their strong similarity and will dramatically show the chemical effect of adding water. Slight differences among the spectra of the hydrolyzed solutions will then be correlated with differences in film quality.

CHAPTER 1.

MATERIALS AND PROCESSING METHODS

Since this investigation is designed to characterize the soluble and insoluble films which can result from the controlled partial hydrolysis of metal alkoxide carboxylates, it is reasonable to begin by assessing the basic materials and methods which control the properties of the films. I will begin with the transition metals themselves, and then proceed to briefly review the nature of colloids and gels, sol-gel processing, alkoxides, carboxylates, and the alcohols, carboxylic acids, and esters which are always involved in the production of our coating solutions. Finally, I will discuss the coating solutions and methods themselves.

1.1. TITANIUM, ZIRCONIUM, AND HAFNIUM

Each of the coating materials generated and studied for this work involves titanium, zirconium, or hafnium. These elements comprise the group IV transition or 'd' block metals in the periodic table. To distinguish the transition metal groups from the main element groups, the CAS nomenclature uses an 'A' to designate the main groups and a 'B' to designate the transition groups; the older IUPAC nomenclature is in conflict with this convention. Throughout the remainder of this document I will refer to the transition group IV elements simply as 'group IV' without further distinction.

Titanium is the most abundant element of the group, making up 63% of the earth's crust. Among all the transition metals, titanium is the second most abundant. Zirconium represents roughly 1.6% of the crust, while hafnium comprises less than 0.03%. However, when compared to other elements, hafnium is no more rare than cesium or bromine (Greenwood and Earnshaw, 1984).

Some of the physical properties of Ti, Zr, and Hf are presented in Table 1. Due to the "lanthanide contraction", the ionic radii of Zr and Hf are virtually identical; the only significant difference between these elements are their densities, transition temperatures, and neutron absorbing abilities (Greenwood and Earnshaw, 1984).

Table 1. Some properties of group IV transition metals.

Property	Ti	Zr	Hf
Atomic number	22	40	72
Number of natural isotopes	5	5	6
Atomic weight	47.88	91.22	178.49
Electronic Configuration	[Ar] $3d^2 4s^2$	[Kr] $4d^2 5s^2$	[Xe]$4f^{14}$ $3d^2 4s^2$
Electronegativity	1.5	1.4	1.3
Metal radius/pm	147	160	159
Ionic radius (6 coord.)/pm M(IV)	60.5	72	71
M(III)	67.0		
M(II)	86		
MP/°C	1667	1857	2222
BP/°C	3285	4200	4450
Enthalpy of fusion/kJ/mole	18.8	19.2	(25)
Enthalpy of vaporization/kJ/mole	425	567	571
Density (25°C) g/cm^3	4.5	6.5	13.28
Electrical resistivity (25°C) μohm cm	42.0	40.0	35.1

(Greenwood and Earnshaw, 1984)

The metals are highly corrosion resistant. Except for hydrofluoric acid, mineral acids have little effect on the dense oxide layer which forms over the metal's surface. The group IV transition metals also exhibit a large range of oxidation states and coordination numbers which are shown in Table 2 (Greenwood and Earnshaw, 1984).

From Table 2, it is apparent that the group IV metals are capable of showing a wide range of complex chemical behavior. It is clearly the richness of this chemistry that will enable us to adjust the properties of our coating materials to suit the needs of specific applications.

1.2. COLLOIDAL SUSPENSIONS AND GELS

A *colloid* has been defined as a suspension of a finely dispersed phase (~1 - 1,000 nm) not significantly effected by gravitational settling, with interaction dominated by short-range forces such as von der Waals attraction and surface charges. The dispersed phase also characteristically exhibits Brownian motion, due to random collisions with molecules of the supporting medium (Brinker and Scherer, 1990).

Colloidal suspensions in a gaseous medium are termed *aerosols*; colloidal liquid droplets in a liquid medium are *emulsions*. A *sol*, distinct from both aerosols and emulsions, is defined as a colloidal suspension of a dispersed solid phase in a liquid medium, where the "solid" can be either *particulate* (non-polymeric) or *polymeric* (Brinker and Scherer, 1990).

Many polymeric systems could also be legitimately considered true solutions rather than sols, and so the terminology chosen often depends

Table 2. Oxidation state, coordination, and stereochemistry

Oxidation state	Coordination	Stereochemistry	Ti	Zr/Hf
-1 (d^5)	6	Octahedral	$[Ti(bipy)_3]^-$	--
0 (d^4)	6	Octahedral	$[Ti(bipy)_3]$	$[Zr(bipy)_3]$
2 (d^2)	6	Octahedral	$TiCl_2$	Layer structures and clusters
	12	--	$[Ti(\eta^5\text{-}C_5H_5)_2(CO)_2]$	
3 (d^1)	3	Planer	$[Ti\{N(SiMe_3)_2\}_2(CO)2]$	
	5	Trigonal bipyr.	$[TiBr_3(NMe_3)_2]$	
	6	Octahedral	$[Ti(urea)_6]^{3+}$	ZrX_3 (Cl, Br, I),HfI_3
4 (d^0)	4	Tetrahedral	$TiCl_4$	$ZrCl_4(g)$ (solid is octahedral)
	5	Trigonal bipyr.	$[TiOCl_2(NMe_3)_2]$	--
		Square pyramidal	$[TiOCl_4]^{2-}$	--
	6	Octahedral	$[TiF_6]^{2-}$	$[ZrF_6]^{2-}$,$ZrCl_4(s)$
	7	Pentagonal bipyramidal	$[TiCl(S2CNMe_2)_3]$	--
		Capped trigonal prismatic	$[TiF_5(O_2)]^{3-}$	$[Zr_2F_{13}]^{5-}$
	8	Dodecahedral	$[Ti(\eta^2\text{-}NO_3)_4$	$[Zr(C_2O_4)_4]^{4-}$
		Square antiprismatic	--	$Zr(acac)_4$
	11	--	$[Ti(\eta^5\text{-}C_5H_5)(S_2CNMe_2)_3]$	
	12	--	--	$[M(\eta^3\text{-}BH_4)_4$

(Greenwood and Earnshaw, 1984)

upon the context. The kinetics must also be considered; a solution of monomers and oligomers may gradually evolve into a polymeric sol, and eventually become a particulate sol or gel. There is no exact time when the polymer becomes large enough for the solution to be considered a sol, and the choice of terminology in describing the initial stage may well depend on the kinetics of the reaction.

A *gel* is a substance characterized by the presence of a continuous solid skeleton wet by a continuous liquid phase. Gels can result from the growth of branched or cross-linked polymers, the entanglement of polymeric molecules, or the formation of particulate networks held together by von der Waals forces. Gels can be clear, cloudy, or opaque, and the liquid phase of the gel can exist as a solution, polymeric sol, or particulate sol. The process of gelation generally begins with the formation of fractal aggregates that grow into clusters that link together, as sometimes described by the theory of percolation, until a spanning cluster extends throughout the sol (Brinker and Scherer, 1990). In polymeric systems, the theory of bond percolation seems most applicable to simple cases where a monomer forms bonds at random between neighboring molecules. Complex chemical systems may not be so easily adaptable to this method of modelling.

When gels are allowed to dry by the evaporation of the liquid phase into a surrounding gas phase, the process is accompanied by significant shrinkage and *xerogels* (xero = dry) result. These xerogels are often highly porous and have been used as catalyst supports and filtering media. Gels can also be dried under supercritical conditions, producing *aerogels* which are significantly less dense than the corresponding xerogels.

1.3. SOL-GEL PROCESSING

A variety of systems which exhibit sol formation and gelation can be very useful in the manufacturing of homogeneous powders, radioactive oxide particles, ceramics (including fibers and multicomponent glasses), films, coatings, and monoliths. The recent popularity of the sol-gel approach is attributed to the demonstration by Yoldas (Yoldas, 1975 and 1977) and Yamane and coworkers (Yamane, et. al., 1978) that monoliths can be made by carefully drying gels. The promise of a structurally solid and useful glass produced at room temperature proved to be more dream than reality, and monoliths remain the least important sol-gel products (Brinker and Scherer, 1990).

Sol-gel systems have been made by a diverse array of inorganic and metalorganic precursors including transition metal esters and salts, aluminates, borates, and silicates. Silicates are the single most common precursors, and alkoxides, in general, are used more than any other starting material for the sol-gel process. The general usefulness of alkoxides results from their reactivity with water; the partially hydrolyzed alkoxides can then react together to form dimers, chains, and rings through condensation reactions which free additional water and allow further hydrolysis (Brinker and Scherer, 1990)

GROUP IV TRANSITION METAL ALKOXIDE SYSTEMS

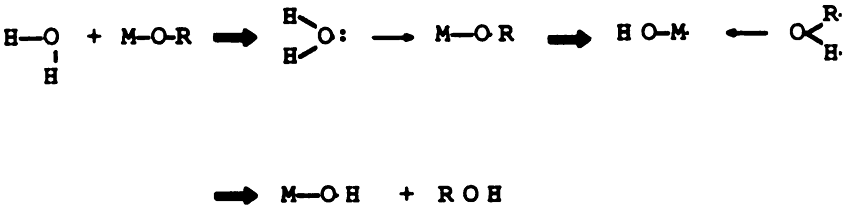
The sol-gel process proceeds through the effect of hydrolysis, alcoxolation, olation, oxolation, alkoxy bridging, and other nucleophilic association mechanisms. Due to the lower electronegativity of these transition metals, the group IV transition metal alkoxides are more susceptible to hydrolysis and condensation than silicon alkoxides.

The suggested mechanisms for these reactions have been summarized in Figure 1 (Brinker and Scherer, 1990). At this point, it should also be noted that olation, as shown in Figure 1, only occurs when the coordination number of the metal has been expanded beyond its oxidation number.

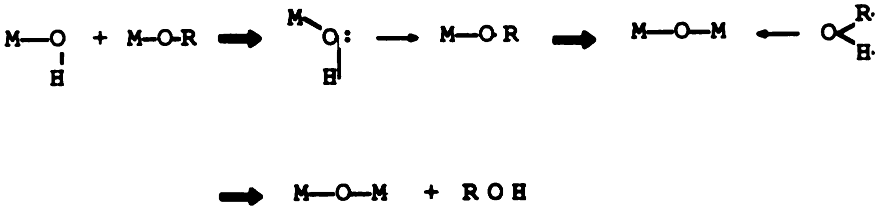
1.4. METAL ALKOXIDES

It has already been noted that industrial applications of metal alkoxides (also named as metal esters) include sol-gel processing of ceramic and metalorganic powders, films, and fibers. However, these important metalorganic compounds are also used as cross-linking agents and catalysts for a variety of organic reactions. Of the group IV transition metal alkoxides, the titanates have undoubtedly been used most frequently for catalysis. Esters and polyesters (Weber, 1962; Jaruzelski and Sheppard, 1963; Stevens and Gardner, 1965; Case,1968; Marzocchi,1972; Haslam, 1958; and Temin and Baum, 1967), polysiloxanes (Gaillissen and Gancberg, 1956; Madaras, 1958; Kohn and Guez, 1961; Hartlein and Olson, 1972; Rauner and Tyler, 1962), polyolefins (Anderson et. al., 1958; Arnold and Foster, 1960; Coover, 1960; Dawes and Winkler,1964; Sianesi and Caporiccio, 1966; Orzechlowski and MacKenzie, 1967; Hogan and Witt, 1971; Hiroyuki, 1972), polyformamide (Beek and Pijpers, 1972), polycarbonate (Reynolds and Dunham, 1972), and polyurethanes (Lawham, 1965; Smelts, 1969) have all been made via titanate catalyzed reactions (Du Pont, TYZOR Bulletin).

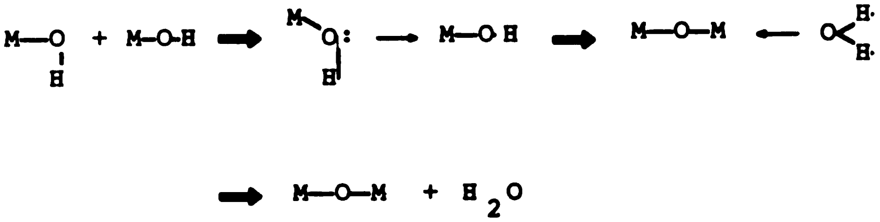
The catalysis of ester formation from alcohols and carboxylic acids plays an important role in the processing of coating materials derived



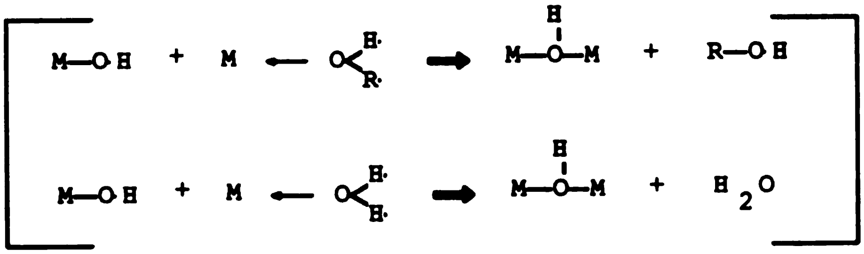
hydrolysis



alcoholysis



oxolation



olation

Figure 1. Sol-gel reaction mechanisms.

from metal alkoxide carboxylates. It is especially important to note that along with the ester, water is generated which can further hydrolyze the metalorganic titanium.

Many group IV 'd' block transition metal alkoxides can be produced by reacting the metal chloride with an alcohol in the presence of ammonia:

$$MCl_4 + 4HOR + 4NH_3 \longrightarrow M(-OR)_4 + 4NH_4Cl \quad .$$

One or more of the alkoxy groups can be changed on an alkoxide by an *alcoholysis* reaction which is often employed to synthesize alkoxides with long or bulky alkoxy groups; alkoxy groups can also be switched by transesterification, in which the new alkoxy group is supplied by an organic ester rather than a alcohol. The overall effect of alcoholysis,

$$M(-OR)_4 + HOR' \longrightarrow (R'O-)M(-OR)_3 + HOR \quad \text{or}$$

$$M(-OR)_4 + 4HOR' \longrightarrow M(-OR')_4 + 4HOR \quad ,$$

can be equivalent to the effect of transesterification:

$$M(-OR)_4 + 4CH_3COOR' \longrightarrow M(-OR')_4 + 4CH_3COOR \quad .$$

When used in alkoxide synthesis, alcoholysis or transesterification is generally driven to completion by removing the product alcohol or ester by azeotropic distillation in an organic solvent. However, it is important to realize that these reactions take place to some degree whenever alcohols or esters are mixed with an alkoxide.

In comparing the isopropoxides of titanium, zirconium, and hafnium, it should be noted that the titanate is a liquid at room temperature, whereas the zirconium and hafnium isopropoxides are solids. It should also be mentioned that, among tertiary alkoxides, volatilities increase in the order Ti < Zr < Hf; due to the bulkiness of their alkoxy groups, these compounds exist as monomeric species -- showing a drastic reduction in the tendency toward coordination expansion and bridging associations (Bradley et. al., 1952 (b)). Normal alkoxides (Bradley et. al., 1953) and shorter chain secondary alkoxides (Bradley et. al., 1952 (c)) show higher values of molecular complexity (degree of oligomerization). The boiling points and degree of molecular association are shown in Table 3 for several alkoxides:

Table 3. Boiling and points and degree of molecular association.

Alkoxide	Boiling point °C/5 mm	Molecular Association
Ti(OEt)	138.3	2.4
$Ti(OPr^i)$	91.3	1.4
$Ti(OBu^t)$	93.8	--
$Ti(OAm^t)$	142.7	1.0
Zr(OEt)	234.8	3.6
$Zr(OPr^i)$	203.8	3.0
$Zr(OBu^t)$	89.1	1.0
$Zr(OAm^t)$	138.4	1.0

(Mehrotra, 1967)

When comparing alkoxides to determine the effect of the central metal on molecular complexity, zirconium and hafnium were found to produce a greater tendency toward oligomer formation than titanium. This was attributed to the larger size and maximum covalency of the heavier atoms since the oxygen-metal intermolecular binding is thought to be quite similar for these metals (Bradley et. al., 1952). The characteristics of the titanium, zirconium, and hafnium alkoxides have been studied and reviewed by Bradley and coworkers in several early sources (Bradley and Wardlaw, 1951; Bradley et. al., 1952 (a, b, c), 1953, and 1978). Excellent reviews by Mehrotra (1967) and Livage and coworkers (1988) also contribute to this area.

1.5. METAL CARBOXYLATES

Metal carboxylates are also known as soaps. Titanium, zirconium, and hafnium carboxylates can be produced by reacting the carboxylic acid anhydrides with an appropriate metal alkoxide (Mehrotra, 1967). Generally, tetrasoaps cannot be obtained from the reaction of a carboxylic acid with these alkoxides because of the tendency to form oligomers. As alcohol is liberated, an ester and water are formed which initiates the oligomer formation. In the case of titanium, oxide-carboxylates tend to ultimately result from this reaction (Mehrotra, 1967).

Zirconium tetrasoaps can also be derived from the reaction of the metal chloride with a carboxylic acid. Since the carboxylates are bidentate ligands, the zirconium is expected to be eight coordinate. When allowed to react with zirconium isopropoxide, carboxylic acids produce a dimer by the following reaction (Mehrotra, 1967):

$$2Zr(OPr^i)_4 + 7RCOOH \rightarrow (RCOO)_3ZrOZr(OOCR)_3 + 7Pr^iOH + RCOOPr^i$$

Some interesting Zirconium IV carboxylate complexes include $Zr(O_2CR)_4$, $ZrO(O_2CR)_2(H2O)_x$, and $ZrO(OH)(O_2CR)(H_2O)_x$. Not surprisingly, the solubility decreases in water and increases in hydrocarbons as the alkyl chain-length increases (Mehrotra, 1983).

Evidently, Ti(IV) tetracarboxylates do not form easily since a large number of attempts to synthesize them had failed before success was eventually attained. Several mixed carboxylates have also been isolated: $(o\text{-}OC_6H_4CO_2)Ti(OPr^i)_2$, $(o\text{-}HOC_6H_4CO_2)_2Ti(OPr^i)(O_2CR)$, and $(o\text{-}HOC_6H_4CO_2)Ti(OPr^i)(O_2CR)_2$, where $R=C_{11}H_{23}$, $C_{15}H_{31}$, and $C_{21}H_{43}$. Heterocyclic Ti(IV) carboxylates have also been reported having a structure described by: $(Pr^iO)_{4-n}TiL_n$, where n=1-3 (Mehrotra, 1983). Both Ti(II) and Ti(III) carboxylates also exist, and many of these compounds are darkly colored (Mehrotra, 1983).

1.6. ALCOHOLS, CARBOXYLIC ACIDS, AND ESTERS

The reactions used to generate the alkoxide carboxylate coating solutions involve, as reactants or products, several organic compounds. These compounds are alcohols, carboxylic acids, and esters, and some of their important properties should be discussed.

It is commonly known that in aqueous solution the acidity of an alcohol decreases as the alkyl chain length increases. Although this phenomenon has been incorrectly attributed to an inductive effect in some older organic chemistry textbooks, it can more properly be explained by differences in the solvation energy of the anion. In dimethyl sulfoxide, a poor solvating agent for anions, the acidities are equivalent (Allinger et. al., 1976). It is also interesting to note the intrinsic acidity of alcohols in the gas phase shows that the acidity increases slightly with the length of the alkyl chain (Brauman and Blair, 1968). A similar trend can be observed among carboxylic acids. The intrinsic acidity in the gas phase increases from acetic to propionic to butyric acid. While, in aqueous solution, acetic acid is strongest and propionic acid is weakest among the three acids (Jen and Thomas, 1975; Yamdagni and Kebarle, 1973). Furthermore, it is important to note that the insoluble metalorganic coating solutions are predominantly solvated by excess carboxylic acid and are not expected to act like aqueous solutions.

The structures, names, and boiling points of some common alcohols, carboxylic acids, and esters have been given in Table 4. The boiling

Table 4. Structures and normal boiling points for selected alcohols, carboxylic acids, and esters.

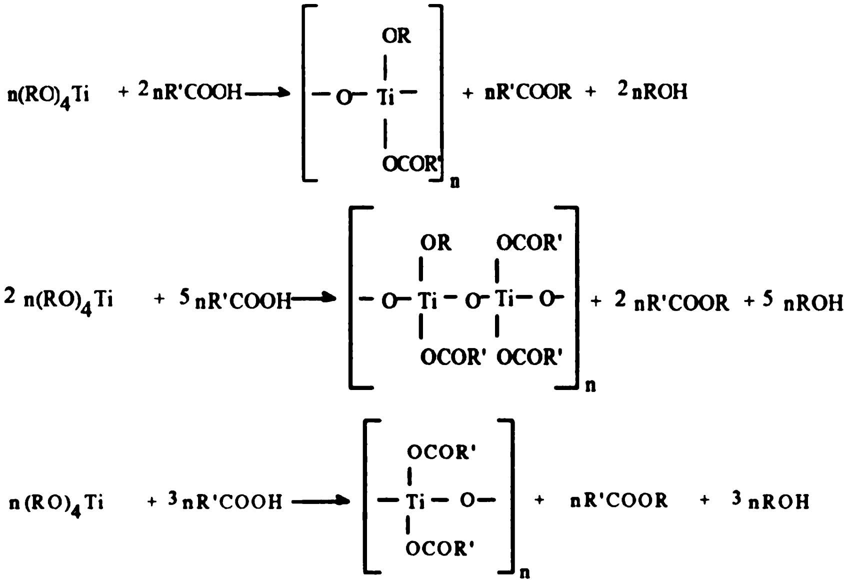
Name	Structure	Normal Boil Point
Methanol	CH_3OH	64.7
Ethanol	CH_3CH_2OH	78.3
n-propanol	$CH_3CH_2CH_2OH$	97.2
iso-propanol	$CH_3CH(OH)CH_3$	82.3
n-butanol	$CH_3(CH_2)_3OH$	117.7
iso-butanol	$(CH_3)_2CHCH_2OH$	107.9
sec-butanol	$CH_3CH_2CH(OH)CH_3$	99.5
t-butanol	$(CH_3)_3COH$	82.5
acetic acid	CH_3COOH	118.
propionic acid	CH_3CH_2COOH	141.
butyric acid	$CH_3(CH_2)_2COOH$	163.
valeric acid	$CH_3(CH_2)_3COOH$	187.
hexanoic acid	$CH_3(CH_2)_4COOH$	205.
octanoic acid	$CH_3(CH_2)_6COOH$	237.
n-propyl acetate	$CH_3COOCH_2CH_2CH_3$	101.6
iso-propyl acetate	$CH_3COOCH(CH_3)_2$	88.4
n-propyl n-valerate	$CH_3(CH_2)_3COOCH_2CH_2CH_3$	167.5
iso-propyl n-valerate	$CH_3(CH_2)_3COOCH(CH_3)_2$	--------

Data on alcohols and carboxylic acids taken from Allinger (1976); data on esters taken from Lange's Handbook of Chemistry, 11th ed. (1974).

points of the alcohols, carboxylic acids, and esters are of general importance to the synthesis of metal alkoxide carboxylates and polyalkoxoacylates because the unwanted reaction products and excess reactants are often removed by distillation. In our work, however, the metalorganic coatings were produced at ambient temperatures and no side products were removed.

1.7. METAL ALKOXIDE CARBOXYLATE DERIVED COATINGS

Among group IV transition metal alkoxide carboxylates, Ti complexes have been studied the most. Two Du Pont patents describe the chemistry involved when the carboxylic acids are mixed with the titanium alkoxides and allowed to react extensively, with or without the addition of water (Feld and Cowe, 1965). Without the addition of water, sufficient reaction leads to metalorganic polymers with 1, 3/2, or 2 carboxylate groups per titanium atom (Langkammerer, 1952):

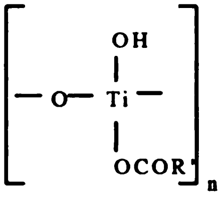


$$n(RO)_4Ti + 2nR'COOH \rightarrow \left[-O-\overset{\displaystyle OR}{\underset{\displaystyle OCOR'}{Ti}}- \right]_n + nR'COOR + 2nROH$$

$$2\,n(RO)_4Ti + 5nR'COOH \rightarrow \left[-O-\overset{\displaystyle OR}{\underset{\displaystyle OCOR'}{Ti}}-O-\overset{\displaystyle OCOR'}{\underset{\displaystyle OCOR'}{Ti}}-O- \right]_n + 2\,nR'COOR + 5\,nROH$$

$$n(RO)_4Ti + 3nR'COOH \rightarrow \left[-\overset{\displaystyle OCOR'}{\underset{\displaystyle OCOR'}{Ti}}-O- \right]_n + nR'COOR + 3nROH$$

The ratio of the combined reactants determines the number of isopropyl groups to be replaced with carboxyl groups. With the addition of a sufficient quantity of water, only one carboxyl side group is retained per titanium atom and the isopropyl groups are replaced by hydroxyl groups (Haslam, 1952):



$$\left[-O-\underset{OCOR'}{\overset{OH}{\underset{|}{\overset{|}{Ti}}}}- \right]_n .$$

In both patents, higher chain-length carboxylic acids are preferred and the waxy products are soluble in organic solvents. When films are cast from these materials, the coating is transparent but soft. The films scratch easily when wiped with a Kimwipe tissue.

The interaction of titanium alkoxides with acetic acid has received special attention due to the interest in using the products as a TiO_2 coating precursor. These films have limited utility in direct applications requiring the unfired film to contact water or organic solvents; however, the films can be used with dry gases. Films made from alkoxide acetates are ideal for applications requiring easily removable or soluble membranes. The formation of these materials are often treated in the context of sol-gel chemistry in which the acetic acid is regarded as a modifier of the metal alkoxide precursor (Livage, 1986; Doeuff, et. al.,1987; Livage, et. al., 1990; Sanchez, et. al., 1988 (a, b) and 1990, Sanchez and Livage, 1990). The acetic acid expands the coordination number of the Ti to 5 and 6, where the acetate groups act as bridging and chelating bidentate ligands (Sanchez, C., et. al., 1988 (a)). Sanchez and coworkers postulate the formation of the

$Ti(OR)_4(AcOH)$ transition state from the nucleophilic addition of the acid followed by the subsequent removal of an alcohol molecule, leaving $Ti(OR)_3(OAc)$ (Sanchez et. al., 1988 (a)). The presence of acetic acid favors polycondensation rather than particulate sol formation. Since the alcohol group is more easily removed by hydrolysis than the acetate group, a greater number of acetates leads to a slower rate of hydrolysis. The first stage of hydrolysis may remove -OR groups while the second stage breaks bridging acetate bonds to form chelating bidentate and monodentate ligands. The final stage of hydrolysis would leave only -OH groups and monodentate acetate groups on the polymer backbone (Doeuff, et. al.,1987).

The formation of complex oxo-alkoxides also proceeds from the reactions of alkoxides and acetic acid. These oxo-alkoxides are thought to develop as side-reaction byproducts which do not participate in the polymerization process (Sanchez et. al., 1990). One such structure which has been isolated and crystallized from the reaction of Ti isopropoxide and acetic acid is $Ti_6(\mu\text{-}O)_2(\mu_3\text{-}O)_2(\mu_2\text{-}OAc)_4(\mu_2\text{-}OPr^i)_4(OPr^i)_6$. This compound is believed to originate from the $Ti_3O(OPr^i)_9(OAc)_3$ trimer which is then believed to release a CH_3COOPr^i molecule leaving $Ti_3(OPr^i)_8(OAc)_2$. The further removal of a $-OPr^i$ by hydrolysis would then be followed by oxolation in which two $Ti_3(OPr^i)_7(OAc)_2OH$ species combine to release two isopropanol molecules and the final oxo-alkoxide product (Sanchez, et. al., 1990). These studies demonstrate the type of chemistry which can be involved in alkoxide and carboxylic acid reactions.

1.8. COATING METHOD AND PRECAUTIONS

The coating solutions are applied to dry, chemically cleaned glass or quartz (Micro cleaning solution) and spun dry at approximately 1100 rpm. This spin-coating technique has been used to produce excellent films from a variety of coating formulations. The coating material probably bonds to the silicon in the surface of the glass via Ti-O-Si linkages; if the coating solution is allowed to age too long before use or if it is prepared at significantly elevated temperatures, the resulting film is softer and shows poor adhesion. Thus, kinetics and processing temperatures are very important. Some properties of the films may also be affected by exposure to UV radiation. Therefore care should be taken to protect the films from long term exposure to light for some applications.

CHAPTER 2.

SPECTROSCOPIC ANALYTICAL TECHNIQUES

Raman and IR spectroscopies have been very useful in characterizing the coating solution. In this section a brief introduction will be provided for these powerful and complimentary vibrational spectroscopy techniques.

2.1. RAMAN AND RESONANCE RAMAN SCATTERING

Raman spectroscopy is still less common than IR absorption, so it will be discussed in somewhat greater detail. Raman scattering provides information which is qualitatively similar to IR absorption: the bands correspond to rotational and vibrational transitions. However, some of the transitions which are quantum mechanically allowed for IR absorption are not allowed for Raman scattering, and vice versa. Thus, the two techniques can be regarded as complimentary rather than redundant. This is especially true for simple, centrosymmetric molecules because their selection rules are mutually exclusive; no transition which is active for one of these two spectroscopy techniques is also active for the other.

Raman experiments require a very bright monochromatic light source which is ideally provided by a laser. Fluid samples are usually illuminated with a light beam oriented 90° with respect to the path toward the collection optics; solid samples are often studied in a 180°, backscattering configuration. Typically, the scattered radiation is directed through a scanning monochrometer to a sensitive detector, such as a photo multiplier tube (PMT), connected to a recording device. Alternatively, the scattered light is taken through a narrow band pass filter (such as a double monochrometer with gratings in subtractive dispersion), then dispersed to illuminate an optical multichannel array (OMA) detector which can analyze the entire spectral region illuminating its surface.

The wavenumbers of the incident radiation ($\tilde{\nu}_0$), a Raman band $\tilde{\nu}'$), and the associated molecular vibrational transition ($\tilde{\nu}_M$) are related such that $\tilde{\nu}' = \tilde{\nu}_0 \pm \tilde{\nu}_M$. When $\tilde{\nu}'$ is greater than $\tilde{\nu}_0$, $\tilde{\nu}'$ is an anti-Stokes band; otherwise $\tilde{\nu}'$ is a Stokes band. Stokes Raman scattering is generally much more intense than anti-Stokes because the Stokes transitions originate from the well-populated ground state; whereas anti-Stokes scattering originates from vibrational excited states which are poorly populated at room temperature in the absence of electromagnetic stimulation. Raman scattering occurs due to an oscillating molecular dipole which is induced by the incident light. Raman active vibrational transitions occur when the vibration involves a change in the polarizability tensor **a**. The induced dipole moment, **P**, depends upon the electric field of the incident radiation, **E**, and **a** such that **P** = **a** • **E**. If Q_k represents the k^th normal coordinate, then the k^th normal mode will be Raman active only if

$$\left(\alpha'_{ij}\right)_k = \left(\frac{\partial \alpha_{ij}}{\partial Q_k}\right)_0 \neq 0,$$

for some element α_{ij} of $\mathbf{a}$. The subscript 'o' denotes evaluation at the equilibrium position, and the term $(\alpha'_{ij})_k$ represents an element in the derived polarizability tensor for the k^th normal coordinate, $\mathbf{a}_k'$.

Resonance Raman scattering occurs when the incident radiation is coincident with an electronic absorption band of the sample. The resulting enhanced signal is 10^3-10^4 times more intense than normal Raman scattering. An explanation of this phenomena using Kramers-Heisenberg-Dirac dispersion theory has been reviewed by Dophin (1978).

2.2. INFRARED ABSORPTION

When light is absorbed in the infrared (IR) region, the energy of the absorbed radiation coincides with the energy required for rotational and vibrational transitions. When observing vibrational transitions in fluid samples, the vibrational bands appear broadened by the closely spaced rotational transitions which occur at each vibrational state.

IR spectroscopy is widely used in the identification of organic compounds. The various functional groups have characteristic absorption bands which aid chemists in determining the structure of an unknown molecular species.

ATTENUATED TOTAL REFLECTANCE (ATR)

Attenuated total reflectance (ATR) spectroscopy allows an IR absorption spectrum to be taken at the surface of an ATR crystal or internal reflection element (IRE). The IR light passes through the crystal, being "internally reflected" back and forth between opposing faces. However, with each "internal reflection", the light protrudes slightly from the surface allowing it to sample the external environment. The depth of the light's penetration depends upon the entry angle and the relative indices of refraction for the ATR crystal and the surrounding medium. This is a very useful technique for examining many samples which would otherwise be difficult to analyze. The "circle cell" configuration is especially useful for testing aqueous solutions with minimal IR absorbance from the water. The theory of ATR spectroscopy and practical information about various ATR configurations can be found in a text by Harrick (1967).

CHAPTER 3.

SOLUBLE COATINGS

3.1. FILMS WITH ACETIC ACID

Soluble coatings have been made from mixtures of acetic acid with titanium isopropoxide, zirconium n-propoxide, and hafnium isopropoxide. The coating solutions were formed by first reacting the alkoxide with acetic acid, and then dissolving the product in water. The aqueous mixtures were then used to coat glass substrates. In general, it was possible to make fairly stable sols from the zirconium and hafnium alkoxides which produced excellent films. The titanate based coating solutions showed a greater tendency to polymerize, and only produced good films when not excessively aged.

3.2. COMPARISON OF GROUP IV METAL ALKOXIDE ACETATES

Although hafnium and zirconium alkoxides with identical alkoxide groups should behave almost identically, it is not surprising that the zirconium n-propoxide showed significant differences from the hafnium isopropoxide isopropanol solvate or isopropanolate which was used to prepare the hafnium-based films. Alcohols are not inert solvents, and they significantly change the reactivity of the alkoxide. Furthermore, the less bulky n-propoxide groups offer less protection to the metal atom allowing a greater tendency toward intermolecular association and coordination expansion and a lower tendency toward linear polymerization. Both the zirconium and hafnium preparations produced films which were superior to titanate derived films.

"HAFNIUM METALLO-ORGANIC FILMS AND GELS PRODUCED BY SOL-GEL PROCESSING"

A comparison of these soluble, sol-gel processed coating solutions and their Raman and IR characterization is contained in a previously published paper (Gagliardi and Berglund, 1989) and is reprinted here in its entirety with the permission of the original publisher:

HAFNIUM METALLO-ORGANIC FILMS AND GELS PRODUCED BY SOL-GEL PROCESSING

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ABSTRACT

Metallo-organic materials are often used as precursors for highly refractory oxides and high-temperature composites. The feasibility of producing hafnium metallo-organic films and gels by sol-gel techniques is demonstrated in the present study. Since hafnium alkoxides are not commercially available, their preparation is an obstacle in the development of their sol-gel processing applications. A common synthesis technique was used to produce hafnium isopropoxide, which was subsequently hydrolyzed under acid catalyzed conditions to produce films and gels. The films were prepared by spin casting and remained optically transparent. Initially, the gels were also optically transparent, but became translucent upon drying. Raman, IR, and light scattering spectroscopies were used to characterize this sol-gel process, and it is compared with the analogous processing of titanium and zirconium alkoxides.

INTRODUCTION

Alkoxides of titanium and zirconium have received increasing interest as precursors for powdered ceramics, sols, gels, and film coatings. Substantially fewer studies have been undertaken with hafnium alkoxides, partly due to the lack of any commercial source. Hafnium oxide films have been made from a hafnium alkoxide using low-pressure chemical vapor deposition (CVD) [1], and ion-sputtering [2]. Our current work is aimed at producing metallo-organic films which can be prepared by sol-gel processing at room pressures and temperatures, and characterizing the process.

Livage has shown that optically clear titanium monoliths can be made from $Ti(O\text{-}Bu^n)_4$ when hydrolyzed with butanol and acetic acid [3]. Clear solutions have been made from the hydrolysis of a zirconium alkoxide with acetic acid [4], and transparent, colorless gels have been made from mixtures of titanium and zirconium alkoxides with acetic acid, water, and metal acetates [5]. In addition, acetic acid has also been used for making films with mixtures of lead, zirconium, and titanium alkoxides [6]. Since acetic acid has been used successfully in these similar alkoxide systems, we investigated the effect of acetic acid on the hydrolysis of hafnium isopropoxide. The isopropoxide was chosen for direct comparison to titanium isopropoxide [3] and for its established synthesis [7-10].

The hafnium isopropoxide synthesis is presented, along with a description of the sol-gel processing for the formation of the sols, gel monoliths, and films. The acetic acid and metal alkoxide systems were compared for hafnium, zirconium, and titanium alkoxides. Light scattering was used to characterize sol stability and gelation rates. Infrared and Raman spectroscopies were used to probe the structure of sols and gels.

MATERIALS AND METHODS

Hafnium isopropoxide was prepared by the direct action of ammonia on hafnium tetrachloride in the presence of isopropanol, as described by Mehrotra [11]:

$$MCl_n + nROH + nNH_3 \quad \text{----->} \quad M(OR)_n + nNH_4Cl$$

The reaction was carried out in excess benzene to keep the product in solution, as in previous syntheses [8,9]. Twenty-five grams of $HfCl_4$ were dissolved in 350 ml benzene and 35 ml isopropanol. The benzene and the isopropanol were dried as described below, and the benzene was added to the $HfCl_4$ prior to the addition of isopropanol. An excess of NH_3 was bubbled through a gas dispersion tube while rapidly stirring the solution. The white NH_4Cl was removed by filtration through a fine glass frit, rinsing the solid with two ~30 ml portions of benzene. The excess NH_3 and solvents were driven off under vacuum with the gradual application of heat. The product was refluxed at ~170°C/0.35mm Hg, but was not purified by distillation. The mixture was then cooled and returned to atmospheric presure. About 60 ml of dry isopropanol was then added and the flask was slowly reheated until the solid melted. As the product was slowly cooled, it formed a wet slurry which could be easily removed from the flask. Although this slurry/paste was used directly in some initial experiments, for subsequent preparations it was transferred to other containers and dried under vacuum to give a white solid. The entire synthesis was performed under vacuum or argon atmosphere to avoid moisture, and the product was stored under argon. The hafnium isopropoxide produced in the manner described still contains isopropanol. Complete removal of the isopropanol requires drying at 120-130 °C under vacuum of 0.5mm Hg [8]. Since the material used in the current study was not dried under these conditions, it should more correctly be referred to as hafnium isopropoxide isopropanolate to reflect the residual isopropanol content.

Titanium isopropoxide, NH_3, and $HfCl_4$ were used as purchased from Aldrich Chemical Company with no further purification. The NH_3 was anhydrous, 99.99% pure, and packaged in a lecture bottle. Zirconium *n*-propoxide was purchased from Alpha Products of Morton Thiokol, with no further purification. However, the zirconium compound had an amber color which was possibly due to an impurity, as further evidenced by the observation of a fluorescent baseline in its Raman spectrum. Isopropanol was refluxed over freshly prepared CaO, distilled, refluxed with magnesium filings, and redistilled just prior to its use. Benzene was refluxed over Na metal until the benzoquinone indicator appeared grayish blue, then distilled as needed. Glacial acetic acid was purchased from Fisher Scientific and used without further purification. Kimax brand microscope slides and commercial grade fused silica windows (1/8"T x 3/4"D) were used as substrates for films and were pretreated by rinsing with acetone. De-ionized water with a resistance of 18 Mohm was used throughout.

INSTRUMENTION

The light scattering experiments were performed on a Coulter sub-micron particle size analyzer, model N4MD. Polystyrene and acrylic cuvetts were used to hold the samples. Raman spectra were collected on a Spex 1877 triple spectrometer using an OMA detector. The Raman spectra were recorded using the 514.5 nm line from an argon laser. The IR transmission spectra were taken on a Perkin-Elmer model 1750 FTIR. The samples were held in a short-path liquid cell holder with NaCl windows.

PROCESSING

(a) Sols and Gels

Gels made from titanium isopropoxide, acetic acid, and water were compared with the zirconium *n*-propoxide and hafnium isopropoxide analogues. In each case, the alkoxide was first mixed with the acetic acid, producing a strongly exothermic reaction which resulted in a colorless, transparent liquid. These mixtures were usually used immediately in the next step of the sol preparation; however, if allowed to age, they all solidified. The hafnium mixture solidified most quickly (< 20 minutes), the zirconium complexes solidified next (~1 hour), and the titanium complexes were slowest to solidify (a few days). The solids formed emit a characteristic ester odor; the generation of an ester during the sol-gel processing of $Ti(O\text{-}Bu^n)_4$ with acetic acid was also noted by Livage [3].

The next step of the process involves combining these complexes with water. If the complex is still in a liquid phase at the time of this addition, it may rapidly solidify, become a white paste, form translucent clumps, or remain a clear liquid -- depending on the type of complex and the molar ratios. As additional water is added, the solid can usually be redissolved. The liquid was passed through a 0.44 micron filter and stored in vials or in capped cuvetts. The basic steps in the sol-gel process are summarized in Fig. 1.

(b) Films

The films were made by spin-casting the solutions described in the previous section. The coating liquid was applied to the surface of the substrate, which was then spun to remove the excess, resulting in a relatively even film. Films were also made by dropwise addition of the liquid onto a spinning substrate, or by angling the surface of the substrate and allowing the excess-coating material to drip off.

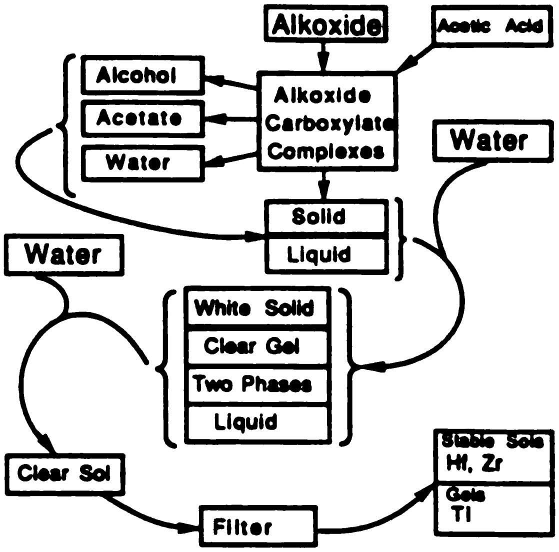


Figure 1. Schematic of Sol-Gel Process

RESULTS AND DISCUSSION

When sufficient acetic acid was mixed with titanium or hafnium isopropoxide, or zirconium *n*-propoxide, a water soluble product resulted. For titanium alkoxides, Livage has described this general complex as $Ti(OR)_x(Ac)_y$ [3]. In the case of zirconium, several carboxylate complexes have been made by reacting alkoxides with carboxylic acids [11]: $((RCO_2)_3Zr)_2O$, $Zr(O_2CR)(OPr^i)_3$, and $Zr(O_2CR)_2(OPr^i)_2$. These compounds are metal carboxylates, and the last two compounds listed are also metal alkoxide carboxylate complexes [11]. For simplicity, the complexes which result from mixing acetic acid with an alkoxide will be regarded as metal alkoxide acetates. TiPA, ZnPA, and HiPA will be used as acronyms for titanium isopropoxide acetates, zirconium *n*-propoxide acetates, and hafnium isopropoxide acetates, respectively.

The titanium-containing sols, produced from TiPA and water, gelled in times ranging from two days to more than a week. The sols derived from hafnium and zirconium never formed solid monoliths if a solid phase was created and then redissolved, providing the sols were made from only alkoxides, acetic acid, and water. Sols from these latter two alkoxides have remained stable for months showing little or no change in particle size as detected by light-scattering. Examples of sols of this type are given in Tables I-III. The acid/alkoxide and the water/alkoxide ratios will be designated r_a and r_w, respectively, throughout the discussion.

Titanium-containing sols with the r_a values of 5.20 and 10.4 evolved into transparent gels for r_w values of 46.3 and 66.1. The compositions of these four sols are summarized in Table I. The solutions with the smaller r_a values gelled several days sooner, and for a given r_a, the solution with the smaller r_w gelled more quickly. The particle growth was apparent from light scattering experiments.

Table II shows the samples studied for the zirconium-type sols. For the sample with an r_a of 1.00, the complex gelled immediately when exposed to a little water and never fully redissolved for a r_w of 51.9. The gel apparently softened and reset at the bottom of the vial. For sols with r_a values of 1.50 and 1.75, the solid complex eventually redissolved, except for some small translucent particles which were only apparent when the vials were gently shaken. The remaining samples, with r_a values ranging from 1.79 to 5.20, all formed entirely clear sols with no visible particles; except for the sol with an r_a of 1.79, none of these samples formed a

TABLE I. Dependance of Gelation Rates on Composition for Sols from TiPA[a]

R_a[b]	R_w[c]	Gelation Time	Average Particle Size
5.2	46.3	~2 Days	~50 nm after the first hour.
5.2	66.1	~5 Days	~22 nm after the first hour.
10.4	46.3	more than 1 week	~12 nm after first hour ~38 nm after 68 hours.
10.4	66.1	longest	~12 nm after 68 hours[d].

[a]Formed solid phase with initial addition of water. [b]Acetic acid/alkoxide molar ratio. [c]Water/alkoxide molar ratio. [d]Counts/sec were initially too low to permit the particle size measurement.

TABLE II. Dependance of Sol Stability on Composition for ZnPA Derived Sols[a]

R_a[b]	R_w[c]	Comments
1.00	51.9	No measurement[d,e]
1.50	51.9	No measurement[d,e]
1.75	51.9	No measurement[d,e]
1.79	20.8	Counts/sec :1.3e4
1.82	13.9	Counts/sec :2.8e4
1.88	13.9	Counts/sec :2.2e4
2.00	17.3	Counts/sec.:1.75e4
3.00	13.9	Counts/sec.:1.00e4
5.20	16.5	Counts/sec.:5.5e3
5.20	46.3	No measurement[f]

[a]We have never observed gelation in Zr alkoxide/acetic acid sols of this type, except when it occurs immediately. [b]Acetic acid/alkoxide molar ratio. Water/alkoxide molar ratio. [d]Formed solid phase upon exposure to water. [e]Never entirely redissolved. [f]Counts/sec. were too low to allow measurement.

TABLE III. Dependance of Sol Stability on Composition for HiPA Derived Sols[a]

R_a[b]	R_w[c]	Comments
11.8	106	particle size: ~60 nm, stable with aging.
5.30	46.5	no size measurement: counts/sec were too low
3.76	108	particle size: ~300 nm, showed slight decrease with aging (~20nm /month)

[a]Formed solid phase with initial addition of water. [b]Acetic acid/alkoxide molar ratio. [c]Water/alkoxide molar ratio.

significant solid phase which then entirely dissolved.

The hafnium sol-gel solutions behaved similarly to those from the zirconium system with the exception that a solid phase always formed during the initial moment of hydration. Significantly higher values of r_a and/or r_w were used for hafnium sols except for the sol with r_a and r_w values of 5.30 and 46.5, respectively. The behavior of both the hafnium and zirconium based sols contrasted sharply with that of the titanium-type sols, which gel over a wide range of compositions.

Hafnium-containing gel monoliths were prepared from hafnium isopropoxide, acetic acid, hydrochloric acid, and isopropanol. Initially, a solid phase was formed which subsequently redissolved. The resulting sols became clear gels within one to two weeks. These gels took on a bluish tint as they aged, presumably due to the greater scattering efficiency of blue light off the small particles.

The titanium-derived gels also took on a bluish tint as they aged and became cloudier than the hafnium gels. Aging of these gels at 70° C in sealed vials, over the period of several days, caused a further whitening of the gels and the formation of a colorless liquid phase surrounding the gels. When shaken, the solid structure was easily destroyed, forming a white emulsion. This emulsion thickened over time, but never set so firmly that vigorous shaking could not produce dramatic shear-thinning behavior.

The sols created were also used in making films on glass and fused silica substrates. The two hafnium-containing solutions with the largest r_a values (11.8 and 5.30, shown in Table III) worked well as a coating material immediately after their preparation, and the characteristics of these solutions did not change appreciably over time. Many of the zirconium-containing mixtures were too viscous to produce an even coating, but the films showed good adhesion. The zirconium sol with r_a and r_w values of 5.20 and 46.3, respectively, provided good films when diluted to slightly lower the viscosity. The titanium-type sols produced very thin films when freshly prepared. However, these sols were in the initial stages of gelation, and the quality of the film was dependent on the age of the sample. The best titanium films from this system were aged for several hours and then diluted slightly with water before being applied. Samples aged for significantly longer periods produced flaky films with poor adhesion. These systems have not been carefully optimized for film coating; however, the hafnium and zirconium films appear to be easier to make, just as the titanium system appears to be better suited for the formation of gel monoliths over a wide range of compositions.

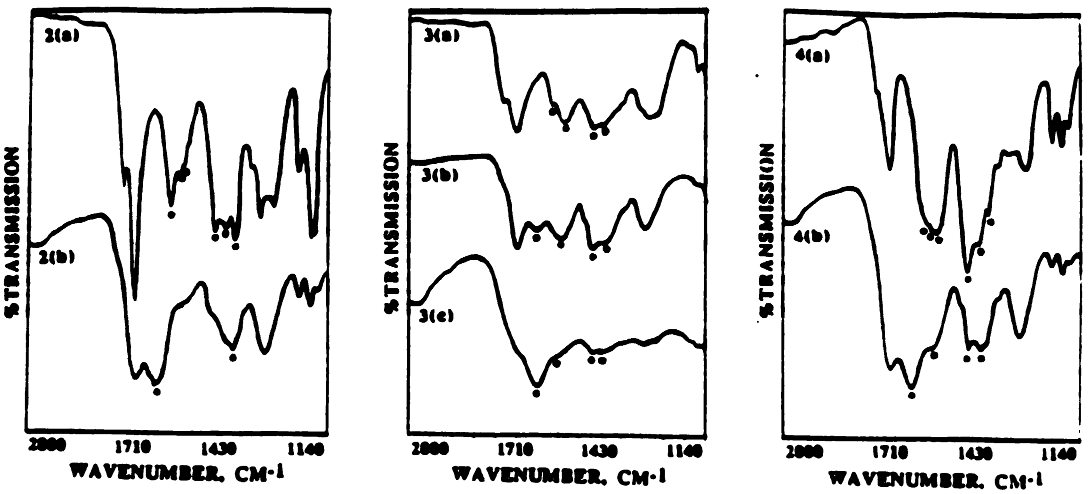
The ester formation which was observed may play an important role in the sol-gel process. If the solidification of the complexes formed from the alkoxide and the acetic acid requires water, it should be noted that water is generated at the same rate as the ester. Alcohols and carboxylic acids are known to react in the presence of mineral acids when heated. The reactivity of primary alcohols is greater than that of secondary alcohols, and the less bulky carboxylic acids are more reactive [12]:

$$\mathrm{RCOOH + R'OH} \xrightleftharpoons{\mathrm{H^+}} \mathrm{RCOOR' + H_2O} \qquad (2)$$

A plausible mechanism for this acid catalyzed reaction has been proposed[12]; however, in the presence of the alkoxide, and in the absence of a mineral acid, this reaction does not necessarily have the same mechanism. If the water is consumed by reaction with the metal, it would drive the reaction forward by removing one of the products and generating one of the two reactants through displacement of either an acetate ion or an ester group from the metal. Water may be a necessary reactant in this solidification since a small amount of water causes immediate formation of a solid phase in many mixtures of titanium or hafnium isopropoxide and acetic acid. Although water may be necessary for solidification, the presence of too much water may actually prevent the formation of a solid phase. This can be seen with initially liquid ZnPT samples that solidify in less than an hour, but do not solidify, or even cloud, when water is added.

The acetic acid and alkoxide derived complexes for titanium, zirconium, and hafnium have been analyzed with infrared spectroscopy before and after the addition of water (Fig. 2-4). The acetate anion may form ionic associations with a metal, or it may bind as a monodentate, chelating or bridging ligand [11,13]. The difference between symmetric and asymmetric CO_2^- stretching vibrations, $[\nu_a(CO_2^-)-\nu_s(CO_2^-)] = \Delta$, occurs within a characteristic range for each type of acetate ligand [13]. This characteristic has been used by Livage to conclude that the complexes formed by mixing acetic acid and $Ti(O\text{-}Bu^n)_4$ are probably characterized by chelating and bridging acetate ligands [3]. After hydrolysis, the samples in Livage's study showed a decrease in Δ, indicating a decrease in the number of bridging acetate ligands [3]. In our study, the titanium complexes, prior to hydration, showed a strong asymmetric stretch at 1599 cm^{-1}, with weak shoulders at 1566 cm^{-1} and 1552 cm^{-1} as shown in Fig. 2a. The symmetric stretch gave a broad band with three peaks at 1447, 1413, and 1379 cm^{-1}. The Δ's thus occurred at 220, 153, and 105 cm^{-1}, indicating that all three types of acetate ligand bonding were probably present, and that the number of monodentate ligands was probably greater than for the conditions studied by Livage [3]. After hydration, strong bands in Fig. 2b appeared at 1646 and 1388 cm^{-1} indicating that Δ has increased to 258 cm^{-1}. This showed that the addition of water further increased the relative number of monodentate ligands, probably by breaking some bridging acetate bonds.

The non-hydrated complexes, of zirconium and hafnium, both demonstrated predominantly bidentate character in their IR spectra shown in the lower sections of Figures 3a and 4a. The peak assignments are given in Table IV. For the hafnium complex, Δ's were found at 100, 150, and 207 cm^{-1}, and for the zirconium, Δ's were found at 96 and 178 cm^{-1}. In the case of zirconium, two different hydrated samples have been examined which yield very different results. A sample with an r_a of 4 was mixed with water in a 1:1 volumetric ratio, yielding Δ's of 109 and 227 cm^{-1}, where the first Δ has been calculated from the more dominant peaks (Fig. 3b). This indicates that both monodentate and bidentate ligands are probably present, with the bidentate ligands predominating. The IR spectrum of the second sample ($r_a = 2.00$ and $r_w = 17.3$) shows the monodentate ligand predominating with $\Delta = 225$ cm^{-1}; the weaker peaks gave a



Figures 2-4. IR spectra of TiPT, ZnPA, and HiPA, before and after the addition of water. TiPA: 2(a) $r_a = 5.2, r_w = 0$; 2(b) $r_a = 5.2, r_w = 46.3$. ZnPA: 3(a) $r_a = 5.2, r_w = 0$; 3(b) $r_a = 5.2, r_w = 46.3$; 3(c) $r_a = 1.75, r_w = 51.94$. HiPA: 4(a) $r_a = 5.3, r_w = 0$; 4(b) $r_a = 5.3, r_w = 46.5$. The "*" indicates bands that are given in Table IV and used in Δ calculations.

Δ value calculated at 110 cm^{-1} (Fig. 3c). The symmetric stretch is very weak in this spectrum. The water-treated hafnium sample ($r_a = 5.30$ and a $r_w = 46.5$) showed a dominant Δ = 233 cm^{-1}, with weaker bands giving Δ = 129cm^{-1} (Fig. 4b). In comparing these systems we see that acetate ligands of all possible types are probably present, in various relative amounts, in most of these samples. One should bear in mind that if this analysis is being applied to sols under highly acidic conditions, or with a high ion concentration, the non-bonded acetate ion would probably have a Δ similar to that of the bridging acetate [13]. Even in a system as complex as this, with three ligand types and free acetic acid present in a single sample, it is relatively easy to study the effect of the composition on the relative predominance of a given acetate ligand. From the zirconium study, it appears that increasing the amount of water, or decreasing the amount of acid, lowers the concentration of bidentate ligands. Neither r_a nor r_w are the same between the two samples which correspond to the spectra in Figures 3b and 3c. However, the relative difference between the r_a values is much greater than that for the r_w; therefore, one could argue that the observed differences between the

TABLE IV. Absorbance Peaks for Calculation of Characteristic Frequency Separation for the Acetate Ligand

	ν_a asymmetric stretch[a]	ν_s symmetric stretch[a]	$\Delta = \nu_a(CO2-) - \nu_s(CO2-)$ characteristic frequency separation[b]	
(TiPA)				
2(a)	1599 (s)	1379 (s)	220	(1)
	1566 (sh)	1413 (s)	153	(2)
	1552 (sh)	1447 (s)	105	(3)
2(b)	1646 (s)	1388 (s)	258	(1)
(ZnPA)				
3(a)	1594 (sh)	1358 (sh)	178	(2)
	1548 (m)	1452 (m)	96	(1)
3(b)	1643 (w)	1416 (sh)	227	(2)
	1561 (m)	1452 (m)	109	(1)
3(c)	1644 (s)	1419 (w)	225	(1)
	1562 (sh)	1452 (w)	110	(2)
(HiPA)				
4(a)	1587 (sh)	1380 (sh)	207	(3)
	1569 (sh)	1419 (sh)	150	(2)
	1556 (s)	1456 (s)	100	(1)
4(b)	1645 (s)	1412 (w)	233	(1)
	1584 (sh)	1455 (w)	129	(2)

[a] The intensity of the peak is indicated by the symbol in parentheses: s=strong, m=medium, w=weak, sh=shoulder. [b] The relative dominance of the ligand-type corresponding to the Δ is shown by the number in parentheses: 1=most dominant, 3=least dominant.

spectra shown in Figures 3b and 3c are predominantly due to the difference in r_a, while the differences between 3a and 3b are predominantly due to the difference in r_w. Increasing r_w had the same effect on the hafnium and zirconium systems.

The Raman spectra for the titanium complex, before and after the addition of water, are compared with the various solvent bands in Fig. 5. The reaction with acetic acid liberates isopropanol and generates isopropyl acetate. Both of these organics have a strong band near 820 cm^{-1} and this band appears in the spectra of the non-hydrated mixture and the sols. The broad peak in the spectrum near 630 cm^{-1}, in Fig. 5c for the non-hydrated sample, probably receives contributions from the acetate δ(O-C=O) and the ν(M-O) of the alkoxide. When water is added, the intensity of this peak is severely reduced as is clearly shown by Fig. 5d, presumably because additional ester groups have been displaced from the titanium by water.

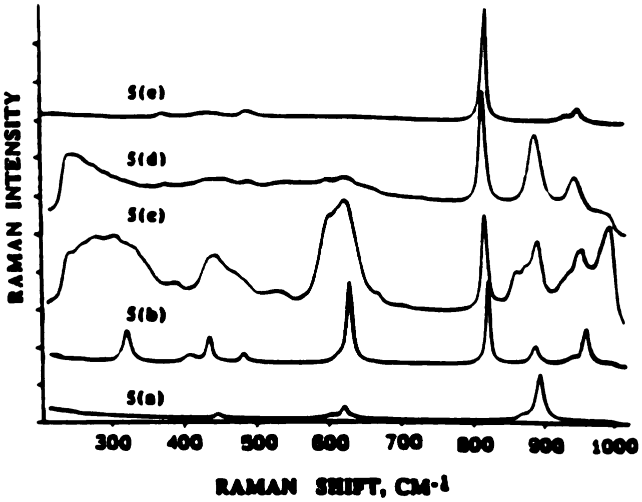


Figure 5. Raman spectra of TiPA, before and after the addition of water, are compared with spectra of some processing reagents and side products: (a) acetic acid; (b) isopropyl acetate; (c) TiPA, $r_a = 5.2$, $r_w = 0$; (d) TiPA, $r_a = 5.2$, $r_w = 46.3$; (e) isopropanol.

A comparison of the Raman spectra of sols prepared from hafnium and titanium (before it has gelled), neat isopropanol, and acetic acid are presented in Fig. 6. The similarity of the spectra for the two sols is striking (Fig. 6a and 6b), and emphasizes the chemical similarity between the two systems. The slight differences in relative band height for the three peaks between 800-1000 cm^{-1} may be due to the additional isopropanol in the hafnium system.

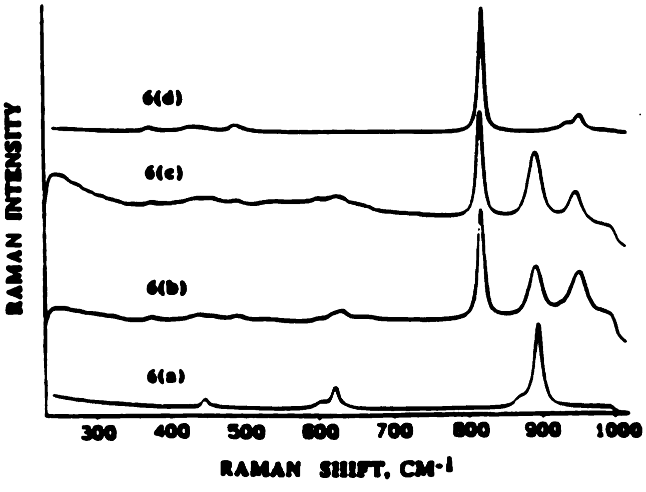


Figure 6. Raman spectra of TiPA and HiPA are compared with one another and with isopropyl alcohol and acetic acid: (a) acetic acid; (b) HiPA + water, ($r_a = 5.3$, $r_w = 46.5$); (c) TiPA + water, ($r_a = 5.2$, $r_w = 46.3$); (d) isopropanol.

The Raman spectrum of the zirconium complex, before and after the addition of water, was compared with the spectrum of neat acetic acid (Fig. 7); the presence of water did not noticeably change the appearance of the spectrum for the zirconium complex, which is especially interesting because this sample did not form a solid when water was added. The generation of water which accompanies the ester generation may offer some explanation for this strange result: the generated water may have already reacted with the system to the extent that additional water caused no further observable changes. It would be interesting to examine the hafnium and acetic acid complex, but the solidification occurred too rapidly. In the case of zirconium, the complex had begun to whiten and solidify soon after the spectrum was finished.

The Raman spectra of the gel monoliths of hafnium and titanium are shown in Fig. 8. These spectra are quite similar, just as the Raman spectra of the sols were similar. The peaks near 820 cm^{-1} indicate that isopropanol and probably isopropyl acetate are trapped in these gels. The metal alkoxide ν(M(O-C)) band near 1029 cm^{-1} is weak in the titanium gel and not apparent in the hafnium gel, indicating that few metal ester groups remain.

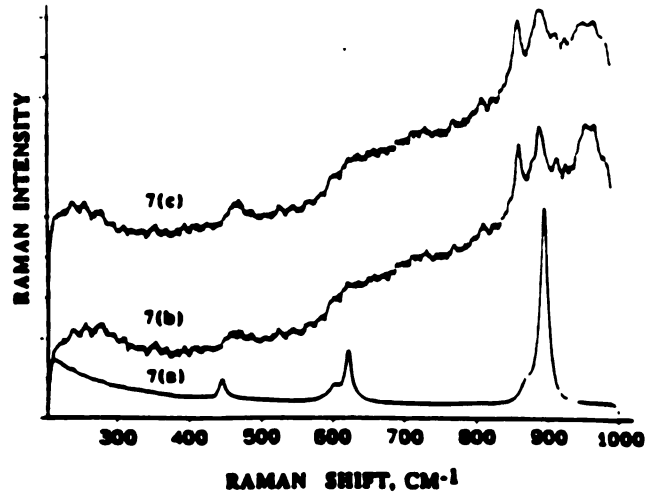


Figure 7. Raman spectra of ZnPA, before and after the addition of water, are compared with the spectrum of acetic acid: (a) acetic acid; (b) ZnPA, $r_a = 5.2$, $r_w = 0$; (c) ZnPA, $r_a = 5.2$, $r_w = 46.3$.

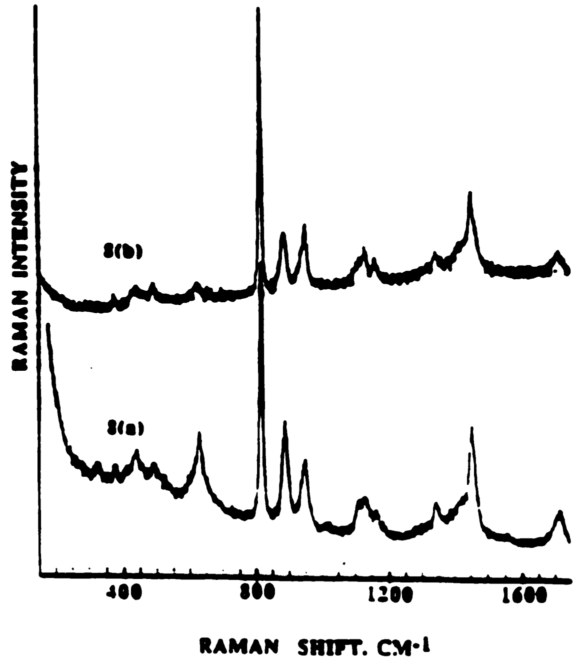


Figure 8. Comparison of Raman spectra for the titanium and hafnium gels derived from TiPA and HiPA , respectively: (a) titanium gel; (b) hafnium gel.

CONCLUSIONS

The sol-gel processing of hafnium isopropoxide can lead to translucent, monolithic gels (when dried) and transparent films . However, this hafnium alkoxide appears to be better suited for the making of films, which are quite sensitive to the exact composition of the sol. Sols made from ZnPA and HiPA by the resolvation of an initially formed solid are quite stable over time, showing no tendency for significant particle growth.

Increasing r_w or reducing r_a appears to reduce the relative number of bidentate ligands. Increasing r_w decreases the gelation time for the titanium system which is contrary to the behavior observed for other similar systems [3].

The spectroscopic evidence for all three systems indicates that acetic acid is active in the coordination chemistry of the metal. Furthermore, the differences in the gel-forming versus film-forming characteristics are probably directly related to the role played by acetic acid. The extension of the current work to organic acids of longer chain and different ligand behavior should allow engineering of systems with widely varying attributes.

ACKNOWLEDGMENTS

The support for this work by the Composite Materials and Structures Center (CMSC) and the Center for Fundamental Materials Research (CFMR) at Michigan State University is gratefully acknowledged. All Raman spectra were taken at the Michigan State University LASER Laboratory. Thanks is likewise extended to Dr. R. B. Lessard and Dr. W. A. Oertling for their helpful discussions.

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CHAPTER 4.

INSOLUBLE COATINGS

4.1. THE ADVANTAGE OF TITANIUM FOR INSOLUBLE COATINGS

Although titanium produced the poorest water soluble films, it clearly makes superior water insoluble and organic solvent resistant coatings. The same characteristics which made it poorly suited for producing stable aqueous sols, allow it to form harder films when processed by other methods. These coating mixtures are distinguished from the water soluble coatings by the use of greater quantities of carboxylic acids and much smaller quantities of water. In these coating mixtures, the carboxylic acid acts as the solvent as well as a reactant.

4.2. PRE-RESONANCE RAMAN CHARACTERIZATION AND THE EFFECT OF VARYING THE CARBOXYLIC ACID CHAIN-LENGTH

In studying the effect of the acid chain length, it became readily apparent that valeric acid produced superior films. However, propionic and butyric acids can also be used, although they are not quite as strong.

"PRE-RESONANCE RAMAN CHARACTERIZATION OF METAL-ORGANIC FILMS FROM TITANIUM ALKOXIDE CARBOXYLATE COMPLEXES"

Our study of the effect of the different carboxylic acids on the quality of the films and on the processing of the materials is also contained in a previously published paper (Gagliardi and Berglund, 1990) and is reprinted here with the permission of the publisher:

PRE-RESONANCE RAMAN CHARACTERIZATION OF METAL-ORGANIC FILMS FROM TITANIUM ALKOXIDE CARBOXYLATE COMPLEXES

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ABSTRACT

Metal-organic films were produced at ambient temperatures and pressures by the controlled hydrolysis of carboxylic acid and titanium isopropoxide mixtures. Pre-resonance Raman spectroscopy was used to study the effect of the organic acid chain length upon the nature of the resulting film. Propionic, butyric, valeric, hexanoic, and octanoic acids were studied, resulting in a proposed correlation between film quality and certain spectroscopic features of the alkoxide carboxylates. The choice of the carboxylic acid and the presence of an appropriate amount of water were shown to be critical in the development of a good film.

INTRODUCTION

Coating materials produced from the controlled hydrolysis of titanium alkoxide carboxylates offer additional versatility and performance over standard sol-gel films. Two patents exist for the manufacturing of acyl-group-containing polymeric titanium compounds from titanium alkoxide and carboxylic acid precursors [1]. In the first of these patents [2], the alkoxide and carboxylic acid mixture is heated under reflux, followed by the removal of alcohol and alkyl ester by distillation. Under these conditions the only water present is that produced by the generation of the alkyl ester, and the resulting polymer is dependent upon the molar ratio (R_a) of alkoxide to acid [1,2]. Thus, $[\text{-O-Ti(OR)(OCOR')-}]_n$, $[\text{-O-Ti(OR)(OCOR')-O-Ti(OCOR')}_2\text{-}]_n$, and $[\text{-O-Ti(OCOR')}_2\text{-}]_n$ represent the polymeric structures resulting from R_a values of 2.0, 2.5, and 3.0, respectively. In the second patent [3], the alkoxide is first reacted with the carboxylic acid, and is then hydrolyzed with additional water. The byproducts of the reaction are removed by distillation as in the first patent, and the polymeric product is reported to have the structure $[\text{-O-Ti(OH) (OCOR')-}]_n$. The materials produced by these methods have found wide application as highly refractive coatings for glass and other substrates, and water-resistant, protective films.

The materials currently under investigation do not require refluxing at elevated temperatures or the removal of reaction byproducts by distillation; the procedure is thus more direct and cost effective. The resulting films are likewise optically transparent and water resistant. In the two patents previously referenced, longer chain length carboxylic acids are preferred. In the current work, relatively short chain length acids are the objects of study.

MATERIALS AND INSTRUMENTATION

The titanium isopropoxide and the carboxylic acids (propionic, butyric, valeric, hexanoic, and octanoic) were obtained from the Aldrich Chemical Company and used without further purification. The microscope slides, which were used as substrates for the films, were standard, pre-cleaned slides manufactured by VWR Scientific Inc.. All water was de-ionized, with a resistance of 18 Mohm.

Raman spectra were collected with a Spex 1877 triple spectrometer equipped with a diode array detector using the 363.8 nm line from an argon laser. Samples were held in quartz cuvettes fitted with Teflon caps.

EXPERIMENTAL PROCEDURE

The liquid carboxylic acid (propionic, butyric, valeric, hexanoic, or octanoic) and the titanium isopropoxide were first combined in a glass scintillation vial and thoroughly mixed with a vortex mixing device. The samples were made with the molar ratios described in Table I such that each sample had a total volume between 3 and 5 ml. For those samples requiring water, the water was added next and the sample was again thoroughly mixed. Films were then spin-cast on glass substrates by wetting the top surface of the glass and then spinning it about an axis perpendicular to the wetted surface. The glass slides were always centered about the axis of rotation, and they were allowed to spin for at least 5 minutes for sufficient drying.

Lauric acid and titanium isopropoxide mixtures were also studied to determine the effect of adding small amounts of lauric acid to the coating solutions previously described. In this study, varying amounts of lauric acid were added to the alkoxide, and Raman spectra were taken of the resulting solution.

TABLE I. Composition of coating solutions and description of resulting films[a].

Acid	R_a[b]	R_w[c]	Film Description
Propionic	2.5	0.0	extensive cracking, flaking
Propionic	10.0	0.0	extensive cracking, flaking
Butyric	2.5	0.0	extensive cracking, flaking
Butyric	10.0	0.0	moderate cracking, flaking on edges
Valeric	2.5	0.0	extensive cracking, flaking
Valeric	10.0	0.0	moderate cracking, flaking on edges
Hexanoic	2.5	0.0	extensive cracking, flaking
Hexanoic	10.0	0.0	slight cracking, slight shrinkage at edges, soft
Octanoic	2.5	0.0	slight cracking, moderate shrinkage at edges, soft
Octanoic	10.0	0.0	never hardens, evaporates over time
Propionic	2.5	1.4	extensive cracking, flaking
Propionic	10.0	1.4	moderate cracking, slight flaking on edges
Butyric	2.5	1.4	extensive cracking, flaking
Butyric	10.0	1.4	no cracking, good uniformity and adhesion
Valeric	2.5	1.4	extensive cracking
Valeric	10.0	1.4	no cracking, very good uniformity and adhesion
Hexanoic	2.5	1.4	no cracking, extensive shrinkage at edges, soft
Hexanoic	10.0	1.4	never hardens, evaporates over time
Octanoic	2.5	1.4	slight cracking, moderate shrinkage at edges, soft
Octanoic	10.0	1.4	never hardens, evaporates over time

[a]The described characteristics appear much more quickly for the solutions without water. [b]R_a is the molar ratio of carboxylic acid to alkoxide. [c]R_w is the molar ratio of water to alkoxide.

RESULTS AND DISCUSSION

The pre-resonance Raman spectra presented in Fig. 1 show the results of adding small quantities of lauric acid to TiPT. The vibrational band assignments for TiPT have been discussed in several previous papers [4,5,6]. However, due to coupling between C-O and C-C vibrational modes, the band assignments have been difficult to make [6]. The strongest TiPT peaks occur at 1026 cm^{-1} and 1182 cm^{-1}. The peak at 1026 cm^{-1} has been associated with the (C-O)Ti stretching vibration [4]. The infrared assignment for this stretch was given as 1005 cm^{-1} [6]. The band at 1182 cm^{-1} has been taken as predominantly a skeletal stretch similar to the IR peak reported at

1170 cm^{-1} [5]. It is likely that both the 1026 cm^{-1} and 1182 cm^{-1} bands represent coupled vibrational modes; therefore, they should not be expected to agree exactly with literature values for the pure vibrational modes. Discrepancies between the IR and Raman peaks can also be expected due to the different selection rules. The peaks of intermediate intensity at 565 cm^{-1} and 612 cm^{-1} may be taken as the symmetric and antisymmetric stretch of Ti-O, respectively [4,6]. The weak peaks at 1129 cm^{-1} and 852 cm^{-1} agree closely with the IR reported values of 1131 cm^{-1} and 851 cm^{-1} for a coupled C-O stretch and skeletal vibration, and a pure skeletal stretch, respectively. The band at 1182 cm^{-1} diminishes with increasing amounts of acid, and the isopropanol peak at 819 cm^{-1} begins to appear as the iPr-O-groups on the titanium are displaced by carboxylate ligands. The symmetric Ti-O stretch at 565 cm^{-1} also decreases, leaving the other Ti-O stretch at 612 cm^{-1} undiminished. The relative peak intensities of the 565 cm^{-1} and 612 cm^{-1} vibrations appear to change more with the addition of lauric acid than with shorter chain-length acids. This could account for the stabilizing effect of adding small amounts of lauric acid to the other coating mixtures.

Coating solutions and descriptions of the resulting films are presented in Table I. The best film without water resulted from hexanoic acid, R_a = 10.0. With water, the best film resulted from valeric acid, also with R_a = 10.0. The film solutions containing no added water produced less stable films, in general, than those from solutions with added water. However, a particular acid at a given R_a may produce a better film without water than with water as exemplified by hexanoic acid at R_a = 10.0. In general, it might also be said that higher R_a values produce better films than lower R_a values, yet octanoic acid produces better films at the lower R_a, with or without water.

The Raman spectra of 'water free' coating solutions, shown in Figures 2 and 3, look very similar; it appears that all of these carboxylic acids interact with the TiPT in a similar way. The lower R_a

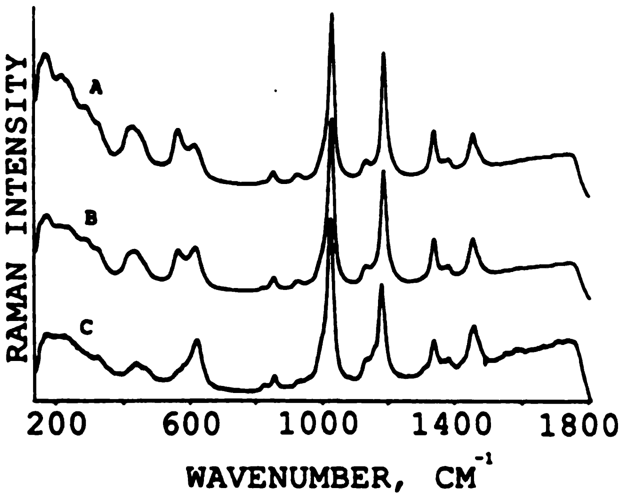

Figure 1. Raman spectra showing the effects of increasing concentrations of lauric acid on titanium isopropoxide (TiPT). (A) Pure TiPT, R_a = 0, (B) TiPT + lauric acid, R_a = 0.12, (C) TiPT + lauric acid, R_a = 0.62. (R_a = the molar ratio of acid to alkoxide.)

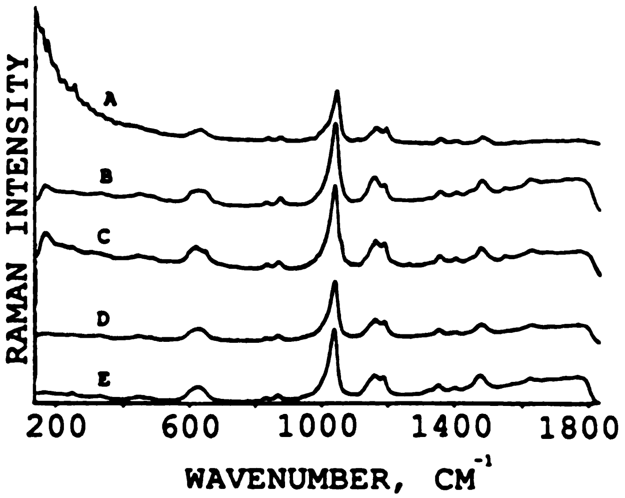

Figure 2. Raman spectra of coating solutions having a low acid molar ratio (R_a = 2.5) and no water. (R_w = 0.0.). Acids used: (A) propionic, (B) butyric, (C) valeric, (D) hexanoic, and (E) octanoic. (R_a = the molar ratio of acid to alkoxide and R_w = the molar ratio of water to alkoxide.)

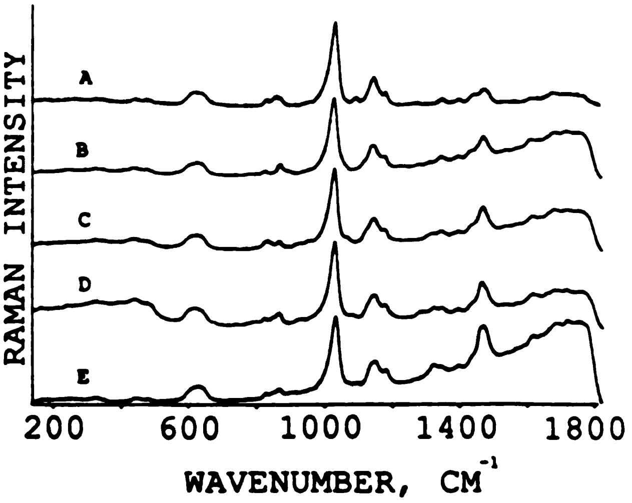

Figure 3. Raman spectra of coating solutions having a high acid molar ratio (R_a = 10.0) and no water. (R_w = 0.0.). Acids used: (A) propionic, (B) butyric, (C) valeric, (D) hexanoic, and (E) octanoic. (R_a = the molar ratio of acid to alkoxide and R_w =the molar ratio of water to alkoxide.)

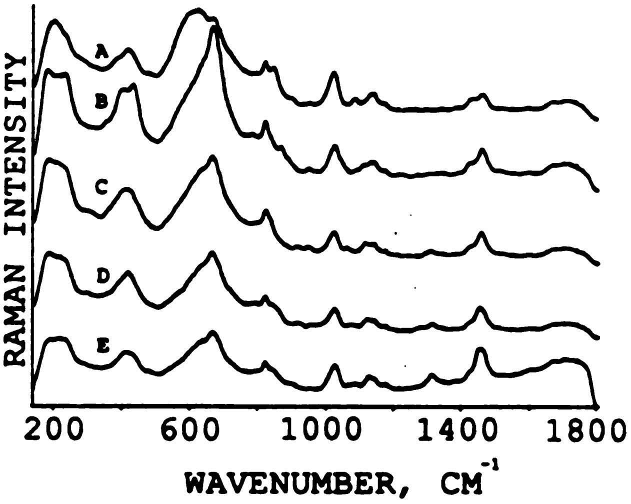

Figure 4. Raman spectra of coating solutions having a high acid molar ratio (R_a = 10.0) and added water (R_w = 1.4). Acids used: (A) propionic, (B) butyric, (C) valeric, (D) hexanoic, and (E) octanoic. (R_a = the molar ratio of acid to alkoxide and R_w = the molar ratio of water to alkoxide.)

solutions are distinguished from the higher R_a solutions by different relative peak intensities for the band at 1182 cm^{-1} . This band is generally less dominant at the higher R_a values. However, there are no features which strongly distinguish between the different carboxylic acids, which shows the great similarity of their reactions with the TiPT.

In Fig. 4, the higher R_W (molar ratio of water to alkoxide) solutions are clearly distinguished from those of the other solutions. In the 'water-free' mixtures there is a fairly symmetrical, broad band near 600 cm^{-1} which contains both the 565 cm^{-1} and 612 cm^{-1} Ti-O stretching vibrations. After the addition of water, this broad band becomes highly unsymmetrical as the 612 cm^{-1} vibration dominates the 565 cm^{-1} vibration. This result shows the dramatic impact that water has on the alkoxide carboxylates and demonstrates part of the role of water in creating a stable film. The band near 600 cm^{-1} appears increasingly unsymmetrical as the chain length decreases, except for the mixture containing propionic acid, which had the least asymmetry. The band appearing near 430 cm^{-1} is also interesting. It appears that the integrated intensity of this band is greatest for butyric and valeric acid mixtures. Thus, the bands near 430 cm^{-1} and 600 cm^{-1} may both be correlated with film quality. The development of these bands may also indicate the degree of polymerization. Another band of interest is the isopropanol band at 819 cm^{-1}. This band appears slightly larger in the butyric and valeric acid coating solutions, indicating that the alkoxide carboxylate complexes formed from these acids may have a greater tendency to release isopropanol, perhaps through greater polymerization. It is also possible that the iPr-O- groups on these complexes are more easily removed by hydrolysis. Thus, it appears that the complexes formed from different carboxylic acids differ in certain aspects of their reaction with water, and these spectroscopically observable differences may by correlated with film quality.

CONCLUSIONS

Pre-resonance enhanced Raman spectroscopy is very useful in studying the differences in the alkoxide carboxylates since it emphasizes the chemistry of the complex over the differences in the vibrational bands of the individual acids. Although the reactions between the acids and the TiPT are very similar, greater differences among the complexes appear after the addition of water. The film-making quality of the solution may be correlated with the asymmetry of the broad band near 600 cm^{-1} and with the integrated intensity of the band near 430 cm^{-1}. The results demonstrate the critical choice of the carboxylic acid and the role of water in achieving good film quality.

ACKNOWLEDGMENTS

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CHAPTER 5.

SUMMARY AND RECOMMENDATIONS

Coating solutions derived from the partial hydrolysis of group IV transition metal alkoxide carboxylates were compared and characterized by spectroscopic analysis. The general sol-gel procedure involved reacting the alkoxide and carboxylic acid, and then forming a sol through the partial hydrolysis of the alkoxy acylate complexes.

Acetic acid was used to produce water soluble coatings. The processing of these materials used larger amounts of water and carboxylic acid than typically incorporated in the production of similar sols, and often involved the rapid formation of an opaque gel which was then resolvated by the further addition of water. This method resulted in stable zirconium and hafnium alkoxoacylate sols which produced excellent films. The titanate produced inferior films and less stable sols which tended to gel. Spectroscopic IR analysis showed that the carboxyl groups were present as monodentate and bidentate bridging and chelating ligands. Larger quantities of water seemed to favor the population of monodentate ligands as was observed by Livage (1986). Light scattering experiments with a particle size analyzer indicated that higher concentrations of water reduced the rate of gelation and the particle size over the concentration range studied for the titanium-based system. This result is contrary to the trends observed by Livage for titanium n-butoxide and acetic acid (Livage, 1986), and offers further evidence that the processing behavior of each system may be highly dependent upon the concentration range of the reactants and the choice of alkoxy ligands. The Raman data from our samples further emphasized the great chemical similarity among coating solutions made from titanium and hafnium isopropoxides. The spectra of the zirconium-based solutions indicate that the zirconium n-propoxide probably contained a highly fluorescing impurity which effectively masked the weaker Raman signal.

Using substantially smaller amounts of water and slightly longer-chain carboxylic acids, water insoluble coatings were produced with titanium isopropoxide. Zirconium n-propoxide produced similar, but less solvent resistant coatings. On this basis, titanium isopropoxide was chosen for a further study on the effect of the carboxylic acid chain length. A survey of carboxylic acids with chain lengths from 3 to 8 carbons indicated that valeric acid produced the best films, although propionic and butyric acids also produced water insoluble coatings of fair quality. Pre-resonance Raman spectroscopic analysis demonstrated the chemical similarity of the materials and showed dramatic changes upon the addition of water. The band associated with the (C-O)Ti vibration (1029 cm^{-1}) is sharply reduced upon the addition of water relative to the largely increased band at 612 cm^{-1} which is associated with the asymmetric Ti-O stretch. This drastic change occurs fairly rapidly upon the addition of water. The degree of asymmetry in the Ti-O stretch and the integrated intensity of a band near 430 cm^{-1} may indicate structural differences which affect the quality of the film. However, it must also be emphasized that the spectral differences are relatively slight, indicating that the major effect of increasing the acid chain length may be an increase in mechanical stability due to the alkyl chain itself. The larger chain may offer support to the matrix like reinforcing fibers in a composite. In this sense, our film materials may be excellent examples of a successful molecular composite.

The next step in this research should be an investigation of the kinetics for the hydrolysis reaction and the associated condensation reactions which follow. An improved understanding of the reactions would also result if the reaction products could be isolated and analyzed at various times during the reaction. Such separation may be achievable through a properly selected column chromatography technique.

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