Synergistic Effect of Driers on Soybean Oil-Based Ceramer Coatings

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Inorganic-organic hybrid coatings were prepared using blown soybean oil with sol-gel precursors. Three sol-gel precursors, titanium tetra-i-propoxide (TIP), titanium (di-i-propoxide) bis (acetylacetonate) (TIA), and zirconium tetra-n-propoxide (ZrP) were used in conjunction with cobalt, manganese, and zirconium driers. The goal of this study was to investigate if a synergy exists between the drier and sol-gel precursors with respect to the autooxidation process. Various coating properties such as hardness, adhesion, reverse impact resistance, and flexibility were evaluated as a function of sol-gel precursor and drier content. Viscoelastic and tensile properties were also investigated.

INTRODUCTION

Seed oils consist primarily of triglycerides of fatty acids. The important fatty acids with respect to film formation are linoleic and linolenic acids. The linoleic and linolenic acids also determine seed oil classification and functionality. The fatty acids react with molecular oxygen via autooxidative crosslinking reactions to form solid polymer films. The autooxidative process has been investigated several times using model compounds. The use of actual triglyceride molecule was not feasible due to the formation of numerous products. The autooxidative drying process involves four separate steps[1-6]: peroxide formation, initiation, propagation (oxygen uptake), and termination, as illustrated in *Scheme* 1. The peroxide formation step is a reaction of singlet oxygen with double bonds to form hydroperoxides with conjugated double bonds. The initiation step involves the decomposition of hydroperoxides into alkoxy (RO·) and hydroxy (HO·) radicals, followed by a hydrogen atom abstraction from doubly allylic methylene groups. The propagation steps include the oxygen uptake and hydrogen abstraction steps. The termination steps are depicted as the crosslinking reactions of radical-radical combinations, which result in film formation.[2]

Soybean oil is classified as a semidrying oil.[7] Soybean oil is typically composed of five types of fatty acids: oleic (~ 25 wt%), linoleic (~ 51 wt%), linolenic (~ 9 wt%), stearic (~ 4 wt%), and palmitic (~ 11 wt%). Raw soybean oil dries very slowly, and has poor coating properties. Therefore, raw soybean oil has to be modified in order to obtain coatings with adequate properties. Blowing oxygen through the soybean oil at an elevated temperature is a method by which soybean oil can be modified. This type of modification increases viscosity and molecular weight, via an autooxidative oligomerization process (*Scheme* 1), while shortening the drying time and ultimately improving film performance. The extent of oligomerization depends on the oxygen flow rate, temperature, and catalyst.

Organometallic catalysts known as driers are added to drying oils to accelerate the drying process, and thereby cure the film as illustrated in *Scheme* 2.[1,3,4] Driers are usually oil soluble metal salts of Co, Mn, or Zr. Cobalt and manganese driers are used as top or surface driers. Top driers catalyze autooxidation predominately at the surface. It was previously supposed that the catalyzing reaction was due to the promotion of hydroperoxide decomposition. However, it has been reported that cobalt salts sensitize the excitation of singlet oxygen, and singlet oxygen has been implicated in the peroxide formation step of autooxidation (*Scheme* 1).[1-4,8,9] Zirconium driers are used as through driers. The reactivity of the through drier is not fully understood, yet a combination of surface and through driers is usually needed to produce a uniformly dried film.

Sol-gel precursors can be added to the drying oil to form inorganic-organic hybrid coatings. The sol-gel precursor forms the inorganic rigid phase of the coating while the drying oil forms the organic flexible phase. Tuman et al. showed that the presence of sol-gel precursor in the organic matrix had a catalytic effect on autooxidation

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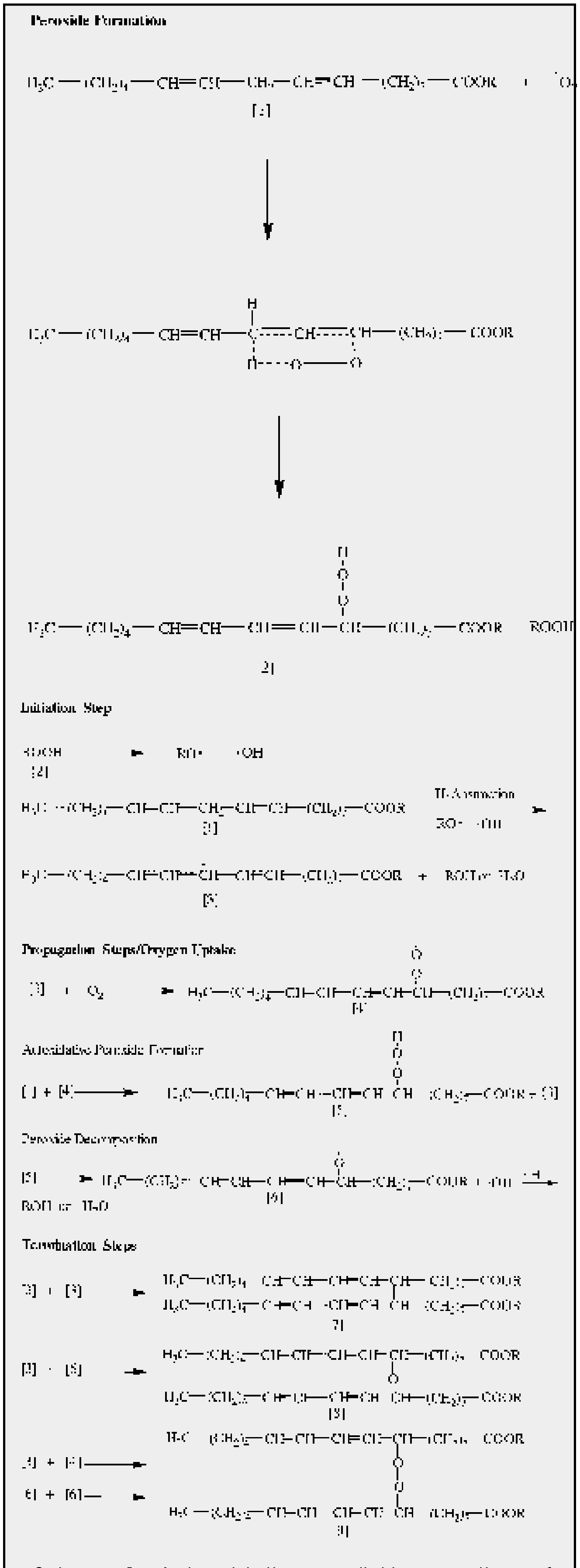
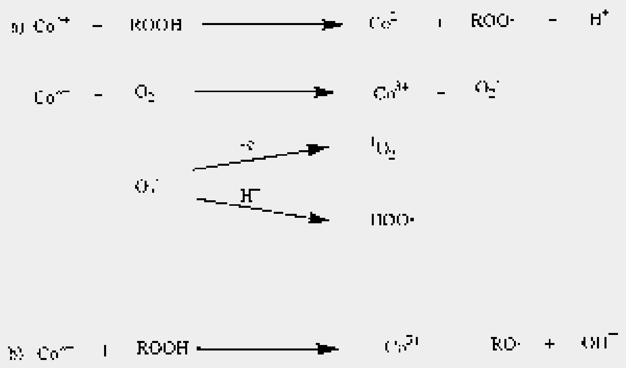
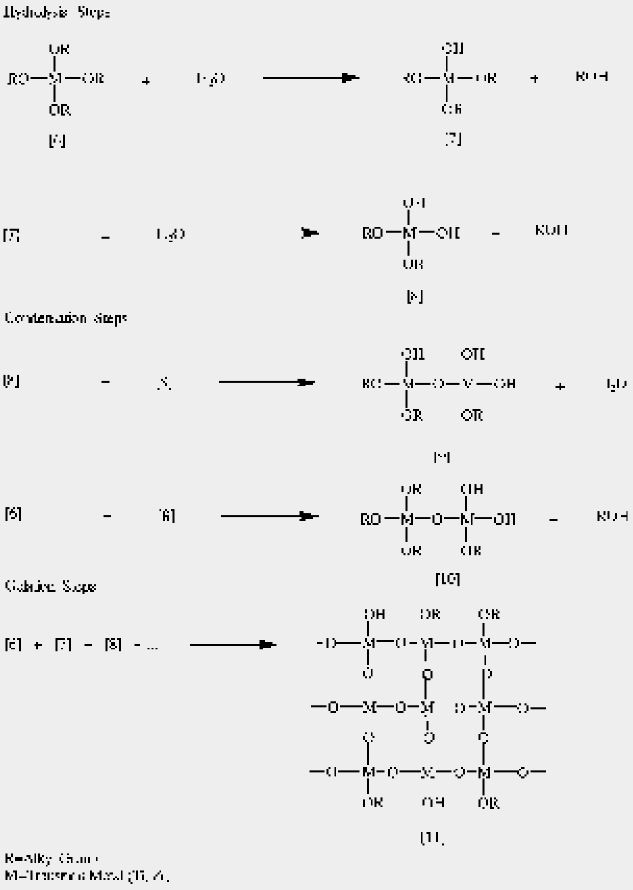


Scheme 1—Autooxidative crosslinking reactions of drying oils.



Scheme 2—Catalytic redox reactions of cobalt driers.

process.[10] Sol-gel precursors form preceramic metal-oxo clusters via sequential reaction with atmospheric water (hydrolysis) and condensation reactions of a metal in an organic matrix as illustrated in *Scheme* 3.[11] Sol-gel precursors need to form metal-oxo-clusters to perform as catalysts. The organic phase reacts with atmospheric oxygen via an autooxidation curing process. Both free fatty acid and peroxides are thought to catalyze the sol-gel precur-



Scheme 3—Sol-Gel Precursor Curing Process.

sor reactions resulting in instantaneous gelation.[12] If the free fatty acid and water content of the oil is high, the addition of sol-gel precursor results in instantaneous gelation.[12]

Recently, inorganic-organic hybrid coatings based on drying oils and alkyd binders were reported by Soucek and co-workers.[10-18] Linseed oil inorganic-organic hybrid coatings were found to have improved anticorrosive protective properties as well as improved mechanical properties.[14] The mixed sol-gel precursors had an interaction effect compared to a single sol-gel precursor based coating which enhanced the mechanical properties.[13] Titanium tetra-*i*-propoxide, titanium (di-*i*-propoxide) bis (acetylacetonate), and zirconium tetra-*n*-propoxide were used as the sol-gel precursors. Tensile strength and modulus of the coatings generally increased with increasing sol-gel precursor content, whereas flexibility and strain-at-break generally decreased.[11]

Inorganic-organic coatings based on blown and epoxidized soybean oil were studied. The blown soybean oil inorganic-organic coatings had improved hardness properties but decreased flexibility.[12] The epoxidized soybean oil ceramer coatings exhibited excellent flexibility and hardness.[15] Linseed oil based hybrid coatings had the best balance between strength and flexibility with titanium tetra-*i*-propoxide (TIP) (5 wt%): Zinc acetate dihydrate (0.5 wt%) content and good corrosion resistance with TIP (10 wt%): Zinc acetate dihydrate (1 wt%) content. Blown soybean oil based hybrid coatings had a significant increase in tensile strength, tensile modulus, and hardness, but suffered a decrease in impact resistance as a function of sol-gel content. The epoxidized soybean oil coatings exhibited increased tensile strength and hardness as the sol-gel content increased. Adhesion and impact resistance decreased as the sol-gel content increased.

The objective of this study was to investigate the effect of driers on the curing and properties of inorganic-organic hybrid coatings. For this study, we used blown soybean oil as the organic phase. The coatings were evaluated for mechanical coating properties, crosslink density, glass transition temperature (T_g), and tensile properties. The overall goal of this research is to develop low volatile organic compounds (VOC) "environmentally-friendly" chromate-free corrosion-resistant primer coatings for metal substrates. These coatings could have specific application in the realm of concrete rebar and pipeline primers.

EXPERIMENTAL

Materials

The soybean oil (ND 551-550) was obtained from Northern Sun-ADM, (Enderlin, ND). The driers (Co, Zr, Mn) as naphthenates in 6 wt% mineral spirit solutions were obtained from OMG and used as received. The sol-gel precursors titanium tetra-*i*-propoxide (TIP) 95 wt% in 2-propanol, and zirconium tetra-*n*-propoxide (ZrP) 70 wt% in 1-propanol were obtained from Aldrich Chemicals Co. (Milwaukee, WI). The titanium (di-*i*-propoxide) bis (acetylacetonate) (TIA) 75 wt% in isopropanol was obtained from Strem Chemicals (Newburyport, MA).

Blowing Process

Approximately four liters of degummed soybean oil was filtered to remove dirt and fine particles and transferred into a five-liter reaction vessel. A thermometer, a condenser, a mechanical stirrer, an oxygen inlet, and an oxygen outlet were fitted onto the reaction vessel. The average oxygen flow rate throughout the blowing process was 636 mL/min. The oil was gradually heated to 137°C, and the temperature was maintained at 137°C for three hours, then the temperature was reduced to 77°C until the completion of the blowing process.[1]

The peroxide and free fatty acid contents were monitored by separately titrating oil aliquots with sodium thiosulfate and potassium hydroxide, respectively. The peroxide and free fatty acid contents of the soybean oil were evaluated via AOCS Cd 8-53 and AOCS Aa 6-38, respectively, according to the American Oil Chemists' society (AOCS) testing procedures. The viscosity was measured with a double-concentric cylinder geometry and a 3.0 s^{-1} shear rate using a Carri-Med CSL-100 controlled stress rheometer at 25°C. The blowing process took 72 hr to complete in this study. The previous study took 51 hr to optimize the blowing process.[1] The optimization criteria was based on a free fatty acid content of ~ 2.6%, peroxide content of ~ 312 Millieq/Kg, water content of ~ 0.18%, and viscosity of ~ 0.57 Pa·s. If the chemical compositions surpassed the optimum values, the oil gelled. On the other hand, if the chemical composition was below the optimum level, the oil imparted poor coating properties.[1]

Coating Preparation

Three types of driers (Co, Mn, Zr) at low (0.05 wt%), medium (0.10 wt%), and high (0.25 wt%) concentrations and at 1:1, 1:2, and 1:3 ratios (Co/Mn, Co/Zr, Mn/Co, Zr/Co, Mn/Zr, and Zr/Mn) were prepared. The driers were optimized by using different combinations, concentrations, and ratios. The formulations were prepared by transferring 10 g of the blown soybean oil into a 20 mL vial and adding the respective drier ratio combination. The vials were mixed on a roll mill for 12 hr. A drawdown bar setting of 6 mils (150 μm) was used to cast the formulations on glass plates for thermomechanical and tensile tests. It resulted an average dry film thickness of 55 μm. Aluminum plates were used for Tukon hardness, pencil hardness, cross-hatch adhesion, reverse impact resistance, and conical mandrel flexibility tests. The aluminum substrates were used in order to compare the data with the data from previous studies. The panels containing the wet films were placed in a dust free chamber for a minimum of 40 hr and maximum of 72 hr until the films were tacky. This allowed the mineral spirits present in the drier solution to evaporate from the coatings. A cure schedule of 130°C, 180°C, and 210°C for one hour at each temperature setting was used. The coatings on glass substrates were cooled to room temperature and removed from the glass using a sharp blade. Soybean oil coatings without drier were prepared for control.

Formulations consisting of 5-15 wt% sol-gel precursors were prepared. The formulations contained 10 g of blown soybean oil with or without Zr/Co drier (1:2 ratio) at 0.45 wt%. The vials were transferred into the dry box. The sol-

Table 1—Fatty Acid Assay, Drying Index, Functionality of Soybean Oil

Fatty Acids and Empirical Autooxidation Features	% Composition of Typical Industrial Grade Soybean Oil and Empirical Autooxidation Data	% Composition or Raw Soybean Oil and Empirical Autooxidation Data	% Composition of Blown Soybean Oil and Empirical Autooxidation Data
Palmitic acid	11	9.9	14.5
Stearic acid	4	4.2	6.1
Oleic acid	25	21.4	28.3
Linoleic acid	51	53.6	42.2
Linolenic acid	9	0.4	0.5

gel precursors were added in the dry box under an argon atmosphere to avoid sol-gel hydrolysis and condensation reactions before the films were cast. The vials were capped, removed from the dry box and placed on a roll mill for only 10-15 min to avoid gelation and also to uniformly mix the formulations. The same procedure and settings used for casting, curing, and handling the drier films were carried out for the hybrid sol-gel formulations. The dry hybrid coatings had an average film thickness of 73 μm. Each sol-gel precursor has its own nomenclature. For example 5 TIP denotes titanium-tetra-*i*-propoxide at a concentration of five weight percent.

Coating Evaluation

Basic coatings mechanical property tests were evaluated according to American Society for Testing and Materials (ASTM) on the hybrid films. Pencil hardness was measured according to ASTM D 3363. Tukon hardness was measured according to ASTM D 1474-85. A Tukon hardness tester uses indentation to evaluate Tukon hardness. The results are expressed in Knoop hardness numbers (KHN) that are related to the weight divided by the area of the indentation:

$$I=L/Ap=L/l^2Cp \qquad (1)$$

where I is Knoop hardness, L is load in kilograms applied to indenter, Ap is uncovered projected area of indentation in square millimeters, *l* is measured length of long diagonal of indentation in millimeters, Cp is a constant relating *l* to the projected area.[19] Reverse impact resistance was measured according to ASTM G 1488. Conical mandrel flexibility was measured according to ASTM D 522. Cross-hatch adhesion test was performed according to ASTM D 3359-87. The pull-off adhesion test involved fastening a bolt with epoxy/amine adhesive perpendicular to the upper surface of the coated sample. An average of six samples was tested for each composition and the average values were recorded.

Tensile properties, stress, strain, and tensile modulus, were measured. The tests were carried out using an Instron universal tester at a strain rate of 20 mm/min. The films tested had a minimum film length of 60 mm, an average width of 11 mm and an average thickness of 0.073 mm. An average of eight samples was tested for each composition and the average values were recorded.

The Dynamic Mechanical Thermal Analysis (DMTA) was carried out with a Rheometric Scientific DMTA 3E. The tests were carried out with parameters of 1 Hz frequency, a temperature range of -100 to 200°C, a heating rate of 3°C/min, a strain of 0.5%, a gap length of 3 mm, an average sample width of 10 mm, and an average sample thickness of 0.064 mm. The test geometry was rectangular tension and compression. The glass transition temperature (T_g) and the crosslink density (M_c or ν_e) were obtained from DMTA analysis. The DMTA spectrum has viscoelastic properties plotted versus temperature. The storage modulus and loss modulus measures the elastic and viscous response, respectively, of the coating film. The ratio of the storage modulus and the loss modulus is known as tan delta. The peak or peak range of the tan delta curve provides the T_g of the coating film. The crosslink density (ν_e) is calculated from the storage modulus vs temperature plot using the following equation:

$$M_c \text{ or } \nu_e=E'_{min}/3RT \qquad (2)$$

where E'_{min} is minimum storage modulus, T (K) is temperature at minimum storage modulus, and R is the universal gas constant.[20] The temperature and the minimum storage modulus data were obtained from the DMTA spectrum.

RESULTS

The primary objective of this study was to ascertain the existence of any beneficial effects of the combination of metal driers and sol-gel precursors in the inorganic-organic hybrid coatings. A blowing process was used to modify the soybean oil. The soybean oil was blown for 72 hr. The peroxide content (~ 350 Millieq/Kg), free fatty acid

Table 2—General Coating Properties of Blown Soybean Oil Coatings

Drier Ratio (wt%)	Pencil Hardness	Crosshatch Adhesion	Reverse Impact Resistance (in·lb)	Conical Mandrel Flexibility (in.)
Blown oil	6B	5B	10	<0.12
0.12 wt% Co/Mn at 1:1	6H	2B	50	<0.12
0.15 wt% Zr/Mn at 1:2	5H	1B	46	<0.12
0.21 wt% Mn/Co at 1:3	5H	2B	68	<0.12
0.45 wt% Zr/Co at 1:2	6H	2B	60	<0.12
0.56 wt% Co/Zr at 1:3	3H	2B	58	<0.12

Table 3—General Coatings Properties of Blown Oil Coatings as a Function of Sol-Gel Precursor and Drier Content

System (wt%)	Pencil Hardness		Crosshatch Adhesion		Reverse Impact Resistance (in·lb)		Conical Mandrel Flexibility (in.)	
	Without Drier	With Drier*	Without Drier	With Drier*	Without Drier	With Drier*	Without Drier	With Drier*
Blown oil	6B	6H	5B	5B	10	10	<0.12	<0.12
5 TIP	3H	3H	2B	1B	10	16	0.94	<0.12
10 TIP	3B	3H	1B	1B	10	10	0.88	0.84
10 TIA	B	3H	0B	2B	14	2	0.47	0.38
5 ZRP	3B	3H	1B	2B	22	14	0.12	<0.12

*Zr/Co 1:2, (0.45 wt% total).

content (~ 2.62%), and viscosity (~ 0.54 Pa·s) were similar to previously reported blown oils prepared by Soucek and co-workers.[1] (See *Table* 1 for features of raw and modified soybean oil.) The sol-gel precursor concentrations of 5 (TIP, ZrP) wt% and 10 (TIP, TIA) wt% were chosen due to the superior overall balance of coating properties found in previous inorganic-organic hybrid coatings studies,[11-13,15] and the 10 wt% TIP was chosen for comparison with the 10 wt% TIA. In addition, a comparison of 5 wt% to 10 wt% TIP was used to evaluate any possible interaction between increasing sol-gel precursor and drier activity. Sol-gel precursor concentrations greater than 10 wt% had produced extremely brittle films and sol-gel precursor concentrations lower than 5 wt% exhibited only a minimal enhancement of properties.

Before the blown soybean oil could be evaluated with sol-gel precursors and driers, suitable drier formulations had to be selected. The drier selection process involved preparing 45 formulations consisting of various combinations of Co, Mn, and Zr driers. The cobalt and manganese were evaluated as top or surface driers and the zirconium was used as through drier. The formulations were cast on aluminum panels and oven cured. Pencil hardness, crosshatch adhesion, reverse impact resistance, and conical mandrel flexibility were measured at ambient conditions, approximately 26°C and 60% relative humidity, as shown in *Table* 2. The drier formulation was selected primarily on the optimal balance of reverse impact resistance, hardness, and cross-hatch adhesion. On this basis, one drier formulation of 0.45 wt% Zr/Co 2:1 was selected. When compared to a drier-free blown soybean oil film the 0.45 wt% Zr/Co (1:2) drier formulation had increased pencil hardness and increased reverse impact resistance, from 6B to 6H and 10 to 60 in·lb, respectively.

After the drier formulation was selected, the blown soybean oil coatings were evaluated as a function of sol-gel precursor content. The mechanical coatings properties of blown soybean oil films as a function of sol-gel precursor and drier content are shown in *Table* 3. In previous studies, the addition of sol-gel precursors resulted in coatings with enhanced hardness, and decreased impact resistance. With the drier, both the 10 TIA and 5 ZrP system exhibited improved pencil hardness, adhesion, and conical mandrel flexibility. The drier decreased the reverse impact resistance for 10 TIA and 5 ZrP by 12 in·lb.

The Tukon hardness was also used to evaluate the inorganic-organic hybrid coatings. The average dry film thickness was 29 ± 5 μm. *Figure* 1 shows the Tukon hardness data for blown soybean oil with sol-gel precursors, and blown soybean oil with sol-gel precursors and driers, respectively. Similar to pencil hardness results, the inorganic-organic hybrid coatings increased in Tukon hardness with increasing sol-gel precursor content. The addition of driers to inorganic-organic hybrid coating significantly improved the hardness for 5 TIP by 37% (5.2 kg/mm^2), 10 TIP by 18% (7.1 kg/mm^2), 10 TIA by 126% (6.1 kg/mm^2), and 5 ZrP by 35% (4.6 kg/mm^2). With the drier, comparing both 5 TIP with 5 ZrP and 10 TIP with 10 TIA, the pairs were all within experimental errors. Discernable differences were not observed (*Figure* 1).

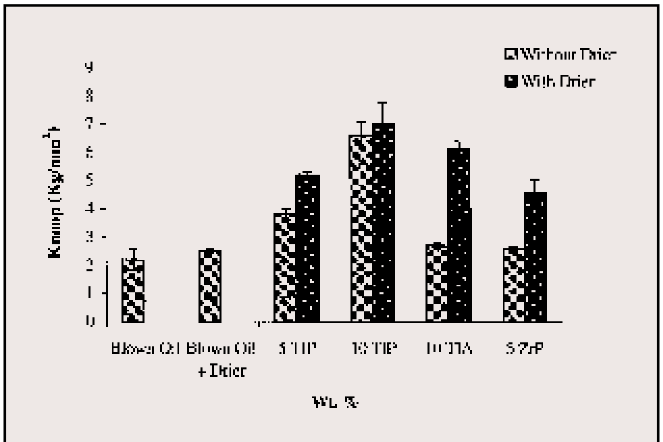


Figure 1—Tukon hardness for coatings produced of soybean oil and sol-gel precursors without and with drier.

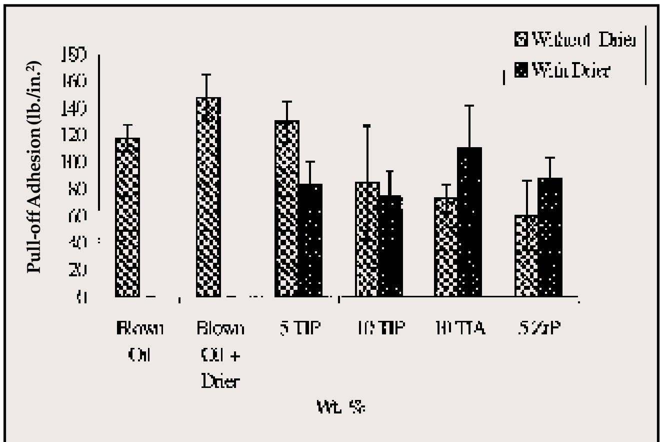


Figure 2—Pull-off adhesion for coatings produced of soybean oil and sol-gel precursors with and without drier.

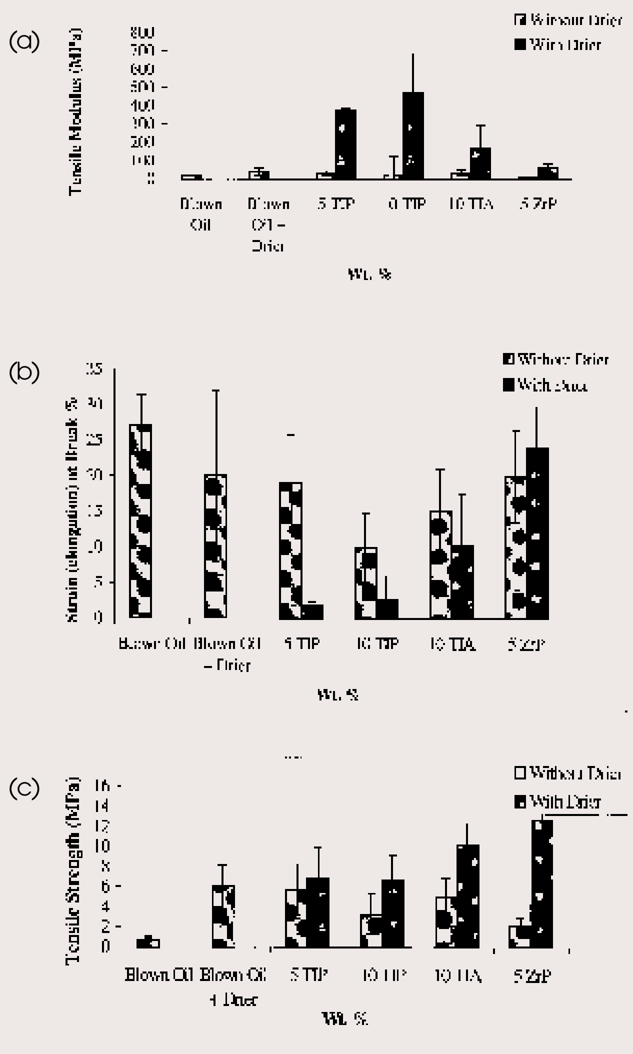


Figure 3—Tensile properties as a function of sol-gel precursor and drier : (a) tensile strength, (b) tensile modulus, (c) strain-at break.

Table 4—Viscoelastic Data of Blown Soybean Oil With and Without Drier

Viscoelastic Parameters	Blown Oil	Zr/Co 0.45 wt% 1:2
T_g (°C)	(10-15)[a] 13[b]	(63-70) 65
E´ min. (Pa)	5.7 × 10^5	8.8 × 10^6
T (°C) at E´ min.	180	165
M_c or ν_e (mol/m^3)	50	803

(a) Range onset and end point.
(b) Midpoint.

Figure 2 shows the pull-off adhesion data for inorganic-organic hybrid formulations without and with drier, respectively. When compared to drier (148 lb/in^2), 10 TIP (85 lb/in^2), 10 TIA (73 lb/in^2), and 5 ZrP (60 lb/in^2) exhibited a decrease in adhesion. The blown oil, drier, and 5 TIP comparisons were within experimental errors. Addition of drier to 5 TIP significantly decreased the pull-off adhesion to 83 lb/in^2. The adhesion of the remaining inorganic-organic hybrid coatings appeared to be independent of drier content. Comparison with drier content of 5 TIP with 5 ZrP and 10 TIP with 10 TIA fell within experimental errors.

Figure 3 shows tensile properties for the inorganic-organic hybrid coatings with and without driers, respectively. As previously reported, the inclusion of sol-gel precursor enhanced the tensile strength and modulus in comparison with the parent oil. It is interesting to note that except for the 5 ZrP formulation, the tensile strength and modulus properties of the sol-gel modified oils without drier were within experimental error of the oil with drier. When the drier was included with the sol-gel precursors, the formulations generally exhibited an increase in tensile strength and tensile modulus and a decrease in strain-at-break. The 5 TIP tensile strength did not increase, making it the exception. The 5 ZrP had the highest tensile strength increase of 505%. Interestingly, both the 10 TIP and 10 TIA had similar increases of 104%. Contrary to the tensile strength values, the 10 TIP exhibited the highest tensile modulus increase by one order of magnitude. The 10 TIA formulation exhibited the lowest tensile modulus increase by 353%. The 5 ZrP exhibited the lowest decrease of strain-at-break by 20%, whereas the 5 TIP exhibited the highest decrease of strain-at-break.

The viscoelastic data was obtained using DMTA. The T_g and M_c or ν_e were calculated from the tan delta (δ) and the elastic storage modulus (E′), respectively. The blown soybean oil, with drier, and inorganic-organic hybrid coatings without and with drier were analyzed as shown in *Tables* 4, 5, and 6, respectively. The inclusion of drier in the blown soybean oil films increased the T_g by 52°C, and yielded crosslink density of 803 mol/m^3. The T_gs of the sol-gel formulations without the drier were all > 25°C except for 5 ZrP. The addition of drier to the sol-gel formulations had a trend in which the T_g and M_c or ν_e of all formulations increased. The 5 TIP and 10 TIP with drier exhibited an increase in T_g over the drier-only formulation by 11 and 6°C, respectively. All formulations with drier and sol-gel precursors exhibited an increase in crosslink density ranging from two to five times over the crosslink density of the individual components.

The tan delta of the films are shown in *Figure* 4. The addition of the drier increased the T_g, and broadened the tan delta peak. This indicated a more tightly crosslinked structure, a nonuniform molecular weight between junction points and nonhomogeneous material (*Table* 4 and *Figure* 4).

Table 5—Viscoelastic Data of Blown Soybean Oil with Sol-Gel Precursors

Viscoelastic Parameters	5 TIP wt%	10 TIP wt%	10 TIA wt%	5 ZrP wt%
T_g (°C)	(21-41)[a] 31[b]	(19-35) 27	(30-37) 34	(4-13) 9
E´ min. (Pa)	7.2 × 10^6	1.1 × 10^7	9.3×10^6	2.0 × 10^6
T (°C) at E´ min.	191	177	171	149
M_c, ν_e, or Reinforcement (mol/m^3)	619	949	836	193

(a) Range onset and end point.
(b) Midpoint.

Table 6—Viscoelastic Data of Blown Soybean Oil with Sol-Gel and Drier

Viscoelastic Parameters	5 TIP wt% + Zr/Co	10 TIP wt% + Zr/Co	10 TIA wt% + Zr/Co	5 ZrP wt% + Zr/Co
T_g (°C)	(66-86)[a] 76[b]	(66-76) 71	(40-61) 51	(60-70) 65
E´ min. (Pa)	2.0×10^7	5.2×10^7	2.7×10^7	1.1×10^7
T (°C) at E´ min.	176	171	184	194
M_c, ν_e, or Reinforcement (mol/m^3)	1770	4700	2345	965

(a) Range onset and end point.
(b) Midpoint.

It was observed that the 10 TIP α-transition was broader than the soybean oil without drier (*Figure* 4). With the addition of drier, the 10 TIP tanδ curve appeared to be a combination of several α-transitions (*Figure* 5). The broad tan delta peak of the film containing the drier was postulated to be a result of partial phase separation of the inorganic and organic phases. Secondary transitions (ß) for the 10 TIP drier formulation were also observed. These were attributed to the crank-shaft motions of methylene unit or carbonyl functional groups.

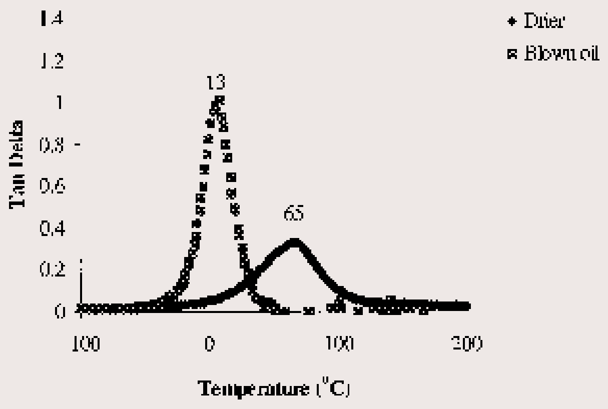


Figure 4—Tan delta of soybean oil with and without drier as a function of temperature.

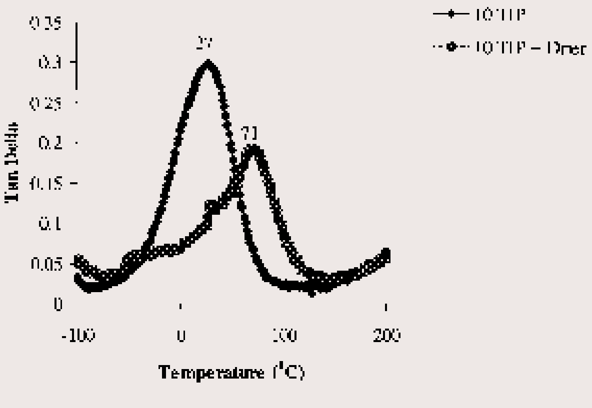


Figure 5—Tan delta of 10 TIP films without and with drier as a function of temperature.

DISCUSSION

In a preliminary study on alkyd ceramers, Sailer and coworkers postulated that the cobalt drier was deactivated via intercalation with TIA into the inorganic phase.[18] *Figure* 6 depicts the drier intercalation into the inorganic phase of the inorganic-organic hybrid coating. If the drier is intercalated into the inorganic phase, it is assumed the drier will be deactivated. It was postulated that the intercalation could be caused by ligand transfer, then reaction with the hydrolyzed sol-gel precursor.[18] If the drier does not undergo substitution, it is assumed that the drier will be located in the organic phase as shown in *Figure* 7. In this case the drier will remain an active homogeneous catalyst.

The increase in crosslink density due to the inclusion of the drier into the soybean oil caused an increase in the tensile strength and tensile modulus. The addition of drier to the soybean oil film enhanced the hardness and tensile features of the film as well as its thermomechanical prop-

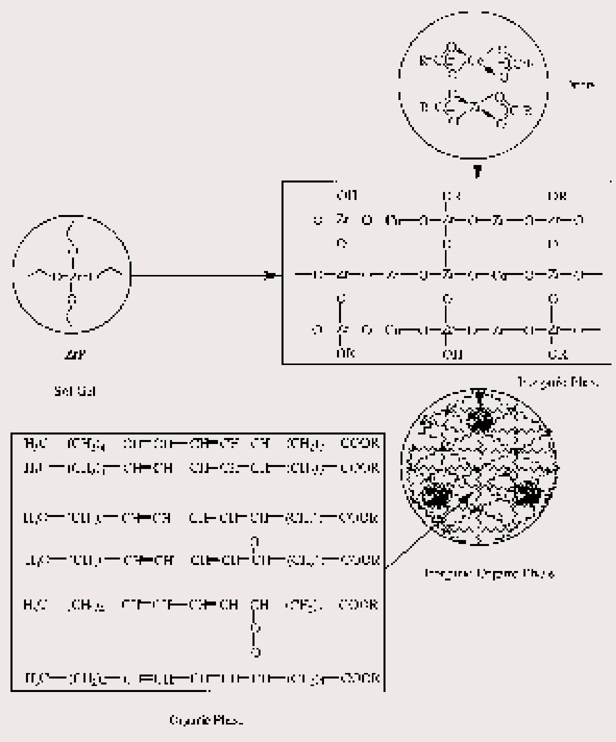


Figure 6—Inorganic-organic hybrid coating with intercalation in inorganic/sol-gel phase.

erties. The T_g increased approximately by +50°C, and formed a substantial crosslink density (*Table* 4).

The addition of the drier to 10 TIP produced slightly higher tensile properties compared to those of 5 TIP, but they were within experimental error. This was probably caused by the increase in crosslink density for the 10 TIP films due to drier presence in the organic phase and the doubling of TIP concentration. The crosslink density of 10 TIP was higher than 5 TIP by 330 mol/m^3 and made the former rigid. This limits chain extensibility and toughness. Contrary to the crosslink density, the addition of drier caused the T_g to decrease slightly by 4°C for 10 TIP. The probable cause was partial phase separation/inhomogeneity of the system. This is possibly depicted as secondary transitions on the tan delta (*Figure* 5). Secondary transitions on the tan delta are features of pigmented systems.

The increase in crosslink density due to inclusion of drier for both the 10 TIA and 5 ZrP was responsible for their respective increases in pencil and Tukon hardness data. The tensile strength data for sol-gel precursors with drier were generally higher than the data for the systems containing only sol-gel precursors. This indicated additional autooxidation of the organic phase by the drier. This also correlated well with the crosslink density data. When compared with the sol-gel precursor only system the 5 TIP, 10 TIP, and 10 TIA had a significant decrease in % strain (elongation) at break, while the 5 ZrP had a slight increase. This was attributed to the high crosslink density due to the inclusion of drier. This decreased the chain extensibility resulting in decreased elongation. The 5 ZrP was an exception. It was postulated that the high reactivity of zirconium sol-gel precursor resulted in the intercalation of the cobalt drier into the metal-oxo-cluster. This intercalation in turn deactivated the drier, which was corroborated by the very low crosslink density and tensile modulus (*Table* 6 and *Figure* 6). The small amount of drier that was in the organic phase and thereby was not deactivated catalyzed the autooxidative reaction and increased the crosslink density. The lack of further crosslinking due to drier deactivation imparted of chain extensibility, thereby enabling 5 ZrP to maintain its strain-at-break (*Figures* 3 and 6; *Tables* 4-6).

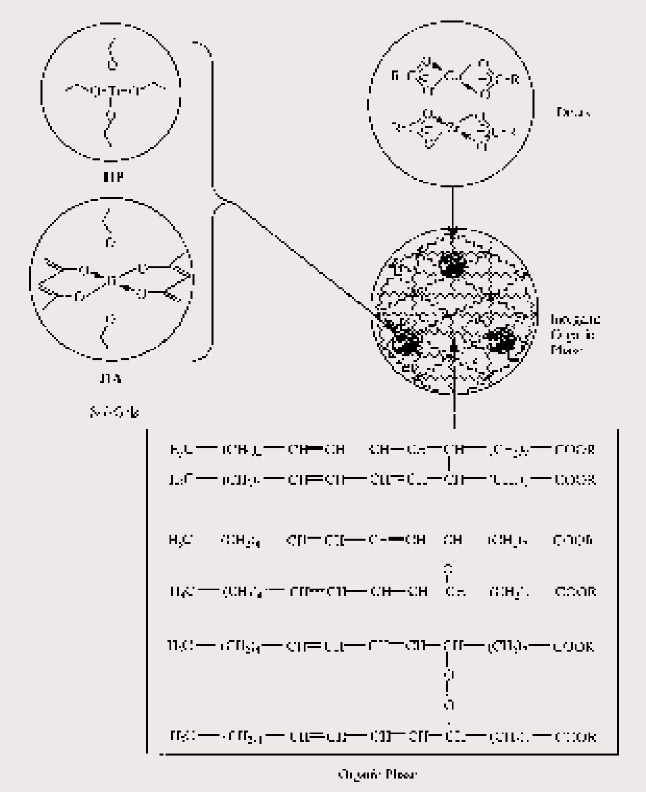


Figure 7—Inorganic-organic hybrid coating with drier in organic phase.

The tensile moduli of the sol-gel precursor plus drier systems of almost all films increased by one order of magnitude, compared to the sol-gel precursor system without drier. The increase in moduli suggests, as expected, an enhancement in the autooxidation of the organic phase. The exception was the 5 ZrP formulation. The T_g of the 5 ZrP with drier was the same as that of the drier optimized film (*Tables* 4 and 6). The ZrP without drier decreases the T_g and crosslink density of the hybrid coating in comparison with the other sol-gel precursors (*Table* 5). The increase in the T_g when drier was added to the ZrP was attributed to the drier activity.

The tensile properties of blown soybean oil films with drier has a trend in which the tensile strength and tensile modulus increased but the strain at break decreased (*Figure* 3). This could be attributed to two factors. One factor is the formation of three-dimensional mixed metal oxide/hydroxide/alkoxide phases as a result of polycondensation. This produces rigid inorganic-organic hybrid clusters. The second factor is the increase in crosslink density of the organic phase due to the inclusion of drier in the hybrid coatings. Generally, the inclusion of sol-gel pre-

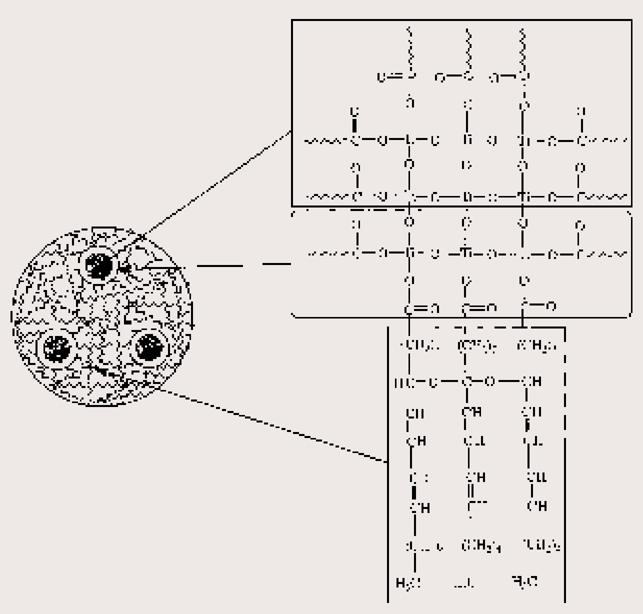


Figure 8—Inorganic-organic interaction of metal-oxo-cluster bonded to fatty acids and crosslinked in the organic phase.

cursor and drier into the drying oil simultaneously contributed to the autooxidation mechanism of the organic phase and enhanced the hardness of the hybrid coatings. The inorganic phase (sol-gel precursor and drier) represents the hard segment and the organic phase (drying oil) represents the flexible segment of the film. The increase in crosslink density for all of the systems brought about by the inclusion of drier was attributed to autooxidation reactions. The possibilities of organic-inorganic (free fatty acid–sol-gel cluster) as well as inorganic-inorganic (drier-sol-gel) interactions exist.[21-22]

All of the films had broad T_g and modulus transitions indicating a broad distribution of chain lengths between network junction points indicating nonuniform molecular weight between junction points. The other possible cause was partial phase separation between organic (soybean oil) and inorganic (sol-gel) phases. The shape and height of the tan delta transition indicates the extent of crosslinking. The higher the tan delta transition the lower the crosslinking and vice versa. The narrow tan delta curve indicates uniform molecular weight between junction points leading to a narrow distribution that indicates homogeneity of the coating. Low crosslink density structure is also indicated by the narrow shape of the tan delta curve (*Figures* 4 and 5).

The enhancement of the hardness and tensile properties when drier was added into inorganic-organic hybrid coatings suggests that the drier was not deactivated by the formation of the metal-oxo-clusters. The viscoelastic properties, in particular the crosslink density, corroborate the drier activity. This evidence implies that the drier remains in the organic phase as a homogeneous catalyst. Furthermore, the reinforcement of the preceramic metal-oxo-clusters and the higher crosslinking that the drier provides in the organic phase results in a synergistic effect for the coatings formulated with 5 TIP, 10 TIP, and 10 TIA. The possible exception is the 5 ZrP formulation. The zirconium sol-gel precursor in the 5 ZrP formulation seems to deactivate the drier. This may be due to the greater reactivity of zirconium. As a consequence, an intercalation mechanism is postulated for 5 ZrP (*Figure* 7).

Although the crosslink density calculation may not be as meaningful for two-phase ceramer systems as in one-phase organic systems, on a relative basis crosslink density calculations are still useful. Debate as to whether the metal-oxo-clusters are very small particles, and therefore should be treated as pigments, is still on-going. An important difference between a titanium-metal-oxo ceramer system and a pigmented system is that the chemical bonding between the inorganic phase and the organic phase exists for ceramers and does not necessarily exist for pigmented systems in drying oil matrix.[21,23] As a matter of fact, the TiO_2 pigmented systems are usually passivated, and the dispersants primarily interact[23] with the pigment surface minimizing resin pigment contact. In addition, since spectral evidence[21] has indicated bonding between fatty acids and the metal-oxo-clusters derived from sol-gel precursors, then perhaps a better model would be to depict the metal-oxo-clusters as a comb, dendritic, or hyperbranched inorganic crosslinking sites as shown in *Figure* 8.

Currently there is no model for accessing the crosslinking density of pigmented coating systems. It is generally accepted that for two phase systems where discrete inorganic particles are in a continuous organic phase, the inorganic phase (i.e., pigment particles) merely acts as reinforcement.[24] This reinforcement of the organic phase usually manifested itself in an increase in tensile modulus, T_g, and observed crosslink density. With respect to crosslink density, it has been proposed that the polymer chains interact with the pigment particle and/or dispersant which in effect shortens the polymers, and therefore enhances the crosslink density.[24] Since this is the current state of the art, crosslink densities of coatings are generally measured without pigment. Using our systems, there is an opportunity to bridge pigmented and unpigmented systems using ceramer coatings.

CONCLUSION

The addition of drier to the sol-gel precursor inorganic-organic hybrid coatings generally improved the coating properties of the blown soybean oil-based ceramer coatings. The inclusion of drier into the inorganic-organic hybrid coatings produced films with higher tensile properties and hardness. The glass transition temperature (T_g) and the crosslink density (M_c) also exhibited substantial increases. The low increase in crosslink density for the zirconium based ceramer coatings was attributed to intercalation of the drier into the inorganic phase deactivating the drier. In contrast, the crosslink density for the titanium based ceramer coatings was increased. Consequently, it was proposed that the drier remained in the organic phase for titanium based ceramer coatings as a possible explanation of the unusually high crosslink densities.

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