Isocyanate-Free Moisture Cure Coatings

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Novel isocyanate-free moisture cure polyurethane coatings with excellent properties have been formulated and evaluated. These coatings utilize polyols derived from the renewable resource soybean oil and its simple derivatives. The coating is autocatalytic and does not require continuous exposure to moisture for the development of full properties. A series of soybean oil-based polyols were synthesized by treating either the raw oil or epoxidized soybean oil (ESO) by a variety of reagents including long chain fatty acids. In a series of model reactions the above polyols were reacted with various diisocyanate compounds, at molar ratio of NCO/OH=1.5:1-3:1 to obtain prepolymers with residual NCO% of around 1.8. The isocyanate-free moisture curable resin was obtained by capping the prepolymer with of aminosilane followed by the addition of a small amount of methanol. Typical clearcoat formulations become tack-free in less than an hour, recoatable in about one hour, and reach a functional cure stage in 24 hr at 40% RH and 25°C.

INTRODUCTION

Among the oldest binders for coatings are naturally occurring triglycerides, triesters of glycerol, and fatty acids found in some vegetable oils including soybean oil. Soybean oil is the most readily available and one of the lowest-cost vegetable oils in the world.[1-2] Both soybean oil and its derivatives are industrially available in large volume and low prices. Traditionally, these oils have been used as raw materials for preparing various resins and coatings such as alkyd resins, epoxy esters, and uralkyd resins, among other industrial uses. While the raw materials are economical and user friendly, the current technology has not been able to produce nonyellowing low VOC alkyd coatings. In recent years, there has been a decline in the coating market share of vegetable oil-based alkyds due to growth of latex paints that have lower VOC, low odor, and ease of clean up.

The nonyellowing problem of conventional alkyd coatings has been substantially overcome with our recent work[3] in a similar project, which primarily uses soybean oil and its derivatives as the main ingredient of both air-dry and heat-cured coatings. Conventional alkyd coatings use metal driers to help in the crosslinking and film formation process. These metal driers are said to have adverse environmental and durability effects. Additionally, conventional alkyd coatings due to the presence of unreacted unsaturated bonds continue air oxidation, which tends to reduce their long-term durability.

The industry is in need of high performance, durable, and nonpolluting vegetable oil-based coatings that can possess the economical advantage and property characteristics of conventional alkyd coatings without the mentioned shortcomings.

The crosslinking and film formation can be accomplished at ambient temperature employing two-component or one-component isocyanate containing moisture cure polyurethane chemistry. While these routes can use soybean oil-derived polyols, they must contain free isocyanate groups either in the form of crosslinker or in the prepolymer.

Isocyanate-free one-component moisture cure polyurethane and adhesive formulations have been prepared by Baghdachi et al. using commercially available polyether polyol resins as precursors.[3]

In this paper, we discuss the novel preparation of isocyanate-free moisture cure coatings in which the resin portion is solely composed of soybean oil and its derivatives. The silane end-capped soybean polyurethane during and after application and upon exposure to ambient

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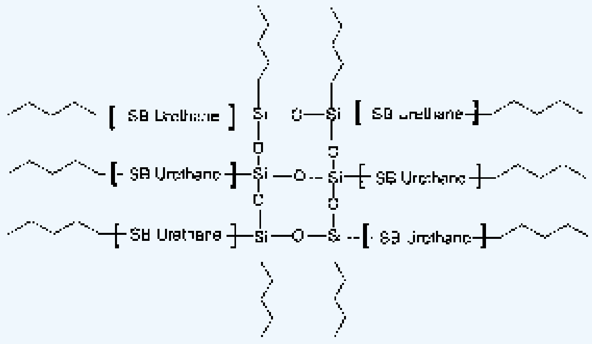

Figure 1—Postulated three-dimensional cross-linked soybean polyurethane.

moisture hydrolyzes rapidly to silanol containing polyurethane compounds. The subsequent condensation produces a highly crosslinked matrix resulting in a tack-free film in a short period of time depending on the temperature and relative humidity (*Figure* 1).

EXPERIMENTAL AND MATERIALS

Epoxidized soybean oil, ESO (Vikoflex 7170Ò, EEW 231) and Fascat 4100 were supplied by Atofina. Soybean oil was supplied by Cargill Company. Pentaerythritol, palmitic acid, 12-hydroxystearic acid, sebacic acid, isocyanatopropyltriethoxy silane, dibutyltin dilaurate (DBTDL), hydroquinone HQ, ethyl triphenylphosphonium bromide (ETPPB), N,N-dimethylformamide (DMF) were obtained from Aldrich Chemical Company and were used as received. Methanol, toluene, and other solvents were all anhydrous grade and were obtained from Aldrich Chemical Company. Tall oil fatty acid (Sylfat FA-3), was obtained from Arizona Chemicals, and soybean oil fatty acid (EMERY 610) from Henkel Corporation. 4,4′-Diphenylmethane diisocyanate (MDI), toluene diisocyanate (TDI), Desmodur N-3300, Desmodur MA 2300, Desmodur E-743 were provided by Bayer Corporation. 3-Aminopropyl-trimethoxy silane (Silquest A 1110) was supplied by the Witco Corporation.

Cypar ™ 9 solvent was obtained from Shell Chemical Company. Iron phosphated steel panels (R-36-I) were obtained from Q-Panel Company.

Preparation of Soybean Oil (SBO) Polyol From Crude Soybean Oil

Procedure A—Preparation of Polymerized Soybean Oil: One hundred grams of soybean oil were charged into a three-necked flask equipped with a thermometer, nitrogen inlet and outlet tube, mechanical stirrer, and water-cooled condenser. The flask was heated to 320-330°C with agitation and held at this temperature under a stream of nitrogen gas for 10 hr. The brownish yellow oil was then cooled to room temperature and discharged. The oil was characterized by titration according to ASTM method D 2340-96, which showed the presence of hydroperoxide, and by viscosity determination and FTIR and GPC.

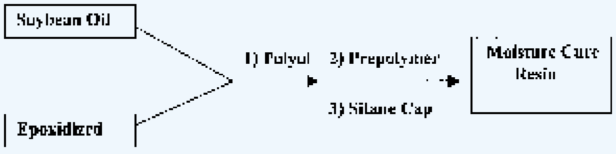

Figure 2—Schematic representation of generalized procedure.

Procedure B—Preparation of SBO Polyol: One hundred grams of the polymerized soybean oil previously mentioned, 12g pentaerythritol, and 0.5 g Fascat 4100 catalyst were added to a three-necked flask equipped with a thermometer, nitrogen purge tube, mechanical stirrer, and water-cooled condenser. The contents were slowly heated to 230°C with good agitation and nitrogen purge and held at this temperature for approximately two hours. After cooling a light yellow polyol was discharged.

Preparation of Polyol from Epoxidized Soybean Oil

Procedure C—One hundred grams of fully epoxidized soybean oil (ESO), 60 g soybean oil fatty acid (SBOFA), and 0.5 g ethyl triphenylphosphonium bromide were charged into a four-necked flask equipped with a thermometer, nitrogen purge tube, mechanical stirrer, and condenser tube. The mixture was slowly heated to 140~150°C, and maintained at this temperature for one hour and then raised to 170°C. The acid value was tested every hour and the heating was ceased once the acid value leveled off at 5 mg KOH/g. Upon cooling a yellowish product was obtained. Similar procedures were conducted replacing SBOFA with palmitic acid and 12-hydroxy stearic acid.

Procedure D—Five hundred grams of ESO and 925 grams of anhydrous methanol were placed in a five-necked kettle equipped with mechanical stirrer, reflux condenser, thermometer, nitrogen gas inlet and outlet, and a dropping funnel. Seventy-five grams of methanol and one gram of borontrifluoride diethyletherate were placed in the addition funnel and the contents of the kettle were heated to 50°C. The borontrifluoride/methanol mixture was added over a 45-min period while maintaining the flask at 60-66°C for another two hours. The contents of the flask were cooled and the methanol stripped under a reduced pressure to afford a light yellow oil.

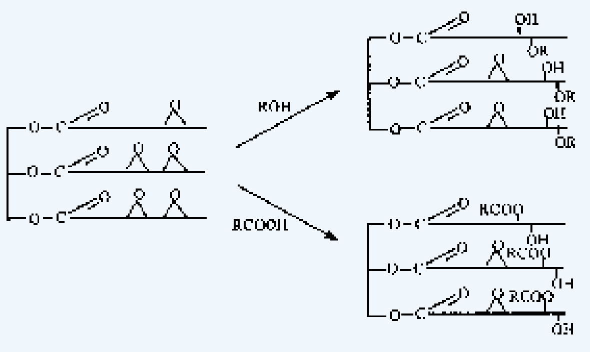

Figure 3—Generalized polyol preparation pathways.

Table 1—Molecular Weights and Polydispersity of Various Polyols

Resin	Mn	Mw	Polydispersity (D)
Transesterification method	1849	25198	13.0
TOFA/ ESO	2050	4550	2.20
ESO (BF3, CH3OH)	1666	1735	1.042

Preparation of Urethane Prepolymer

Thirty grams of ESO polyol (from procedure C using SBOFA) was mixed with 20 g of toluene and loaded into a dropping funnel. Eleven grams of MDI, 34 g toluene and 6g Cypar™ 9 were charged into a four-necked flask equipped with thermometer, mechanical stirrer, nitrogen purge tube, and the above dropping funnel. The mixture was slowly heated to 60°C with good agitation, and the polyol was drop fed over a period of one hour. After the addition was complete, the mixture was kept stirring for another three hours during which time the solution was tested for residual NCO content. Once the drop in NCO was leveled off, the mixture was cooled to room temperature.

Preparation of Isocyanate-Free Moisture Curable Resin

The various prepolymers prepared were treated at room temperature under anhydrous conditions with equimolar amounts of amino silanes, namely 3-aminopropyltrimethoxy silane or 3-aminopropyltriethoxy silane-coupling agents. The reaction mixture, after holding for 15 min, was mixed with 1% anhydrous methanol or ethanol and discharged under anhydrous conditions.

Clearcoat Formulation and Panel Preparation

Prototype clearcoats were made by combining the moisture cure resin, appropriate condensation catalysts, rheology control agents, flow and leveling additives, 1% (w/w based on resin content) anhydrous methanol, and mixed until a homogeneous solution was obtained. The formulations were then applied onto iron phosphated steel, wood veneer, masonry, cold rolled steel, and aluminum panels to obtain a dry film thickness in the range of 25-100 microns. The panels were then placed in a controlled temperature and humidity chamber (30-85% relative humidity) and 25-40°C until tack-free films were obtained. The full testing was conducted after seven days at the specified temperature and humidity.

CHARACTERIZATION

Acid value, hydroxyl value, epoxy content, and NCO content were measured following ASTM D 1980-87, ASTM D 1957-86, ASTM D 1652-90 and ASTM D 2572-91, respectively. Pencil hardness, impact resistance, solvent resistance, adhesion, and flexibility were measured according to ASTM D 3364, ASTM D 2794, ASTM D 5402, ASTM D 3359-95a, and D 0522-92, respectively. The microindentation hardness was tested through modified scanning probe microscope, nanonscope III A instruments. The molecular weight of ESO and polyols were tested on an HP 1047A HPLC-dection-system. Polystyrene was used as a standard. The FTIR spectra were collected on a Nicolet 5107 FTIR spectrometer.

RESULTS AND DISCUSSION

Isocyanate-free moisture cure polyurethane coatings can be prepared using raw or functionalized soybean oil following the generalized method shown in *Figure* 2. Similar polymers and coatings have been prepared and are commercially available using polyether polyols as the starting resin.[3]

Polyol Preparation

To employ soybean oil as raw material for polyurethane reaction, multiple hydroxyl functionality is required. Starting from natural soybean oil, there are two approaches to obtain polyol.

Soybean oil can be thermally polymerized by heating under inert atmosphere[4]; however, the molecular weight distribution of polymerized soybean oil is broad, which results in high polydispersity of around 13.0. Additionally, the polyols are slightly more colored and may not be suitable for clearcoat applications. Small laboratory scale operations require about 10-14 hr processing times.

Another method is the ring opening of epoxidized oils with alcohols, higher polyols, amines, or carboxylic acids

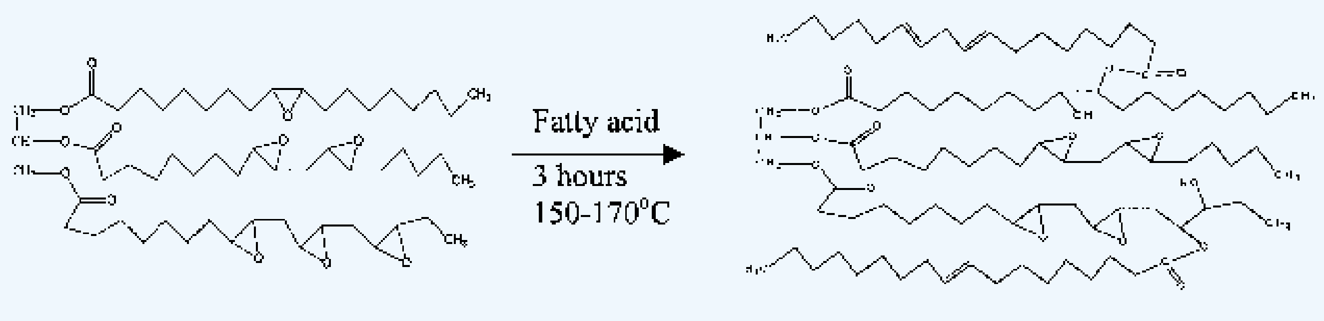

Figure 4—Schematic representation of polyol synthesis.

Table 2—Properties of Various Soybean Oil-Based Polyols

Reagent	SBOFA[a]	Palmitic Acid	12-Hydroxy-stearic Acid	BF3/CH3OH	Transesterification
Acid value	4.9	2.9	3.2	1	10.6
Hydroxyl value	77	81	149.5	170	144
Viscosity (cp, 25°C, 6 rpm)	557	1065	8110	710	12850

(a) SBOFA=Soybean oil fatty acid.

Table 3—Influence of FA/ESO Ratio on % Conversion to Polyols

Polyol	Equivalent Ratio of TOFA / ESO	Final Acid Value	Conversion of TOFA (%)	Reaction Time (hr)	fn of Polyol
A	0.4:1	2.15	96.7	8	1.62
B	0.5:1	4.69	93.0	10	1.95
C	0.6:1	6.33	92.5	10	2.33
D	1:1	27.8	78.8	13	3.31

(a) Ethyl triphenylphosphonium bromide (ETPPB) used as catalyst.

yielding epoxide polyol ethers,[5] derivatized triglycerides,[6] or epoxide polyol esters (see *Figure* 3).

For example, Oldring etc. made acrylated oil which provided good pigment wetting to UV curing formulations for inks and varnishes,[7] by using acrylic acid to open the epoxide ring. Andrew Guo et al., synthesized a soy polyol for rigid polyurethane foams, via the ring opening reaction of ESO and methanol using BF3 /etherate.[8]

Soybean oil-based polyols were also prepared through the ring opening reaction of commercially available epoxidized soybean oil. In this process, the epoxidized oil can be reacted with methanol using borontrifluoride as a catalyst. This process yields low molecular weight, Mn<2000 polyols with narrow polydispersity. While this method consistently produced low molecular weight polyols with high yields, attempts to produce higher molecular weight polyols by this method failed and resulted in semi-solid crosslinked and highly colored materials. Since the process is carried out in methanol, further distillation or evaporation of methanol is needed. In our laboratory, this method has produced consistent results; however, the polyols tend to increase in viscosity upon storage. The processing time typically is in the range of three to four hours excluding the methanol distillation step.

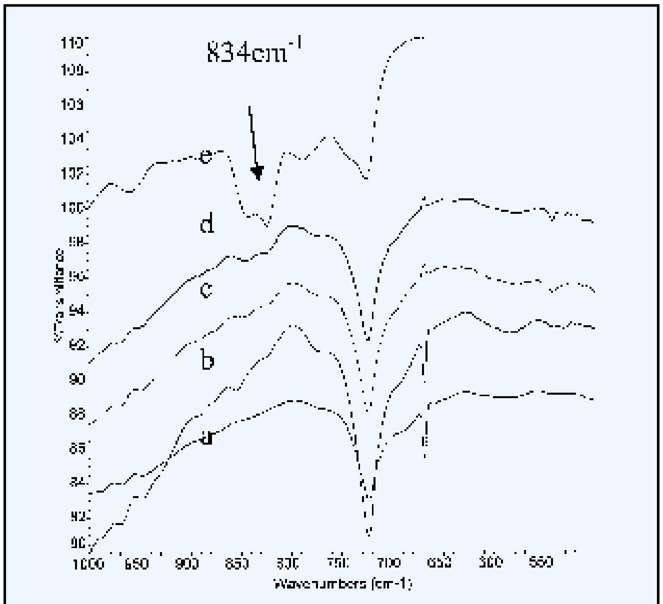

Figure 5—FTIR spectra of ESO and ESO polyols. a: TOFA/ESO=1/1; b: TOFA/ESO=0.6/1; c: TOFA/ESO=0.5/1; d: TOFA/ESO=0.4/1; e: ESO.

We have found that the ring opening reaction of ESO with fatty acids, such as TOFA, can yield polyols with narrow molecular weight distribution and higher molecular weight than the other methods discussed. Generally speaking, an ESO polyol prepared from ESO and TOFA can be obtained within three hours at molar ratio TOFA/ESO=0.6:1, and 0.15% wt triphenylphosphine as catalyst (*Figure* 4).

Using this process, a series of polyols employing long chain carboxylic acids were synthesized and characterized. The properties and physical constants of various polyols are shown in *Tables* 1 and 2.

Factors that have major influence on % conversion, % yield, reaction time, molecular weight, viscosity, and color were systematically investigated. ESO/fatty acid ratio among other factors was found to have the greatest influence on the % conversion of the ESO to polyols. With the increase of the equivalent ratio of TOFA/epoxide, the resulting OH functionality of polyol increases. At equimolar ratio, i.e., TOFA/epoxy=1:1, only 78.8% TOFA was consumed; longer reaction times, higher reaction temperatures did not advance the TOFA conversion. *Table* 3 lists a few of these ratios.

The IR spectra in *Figure* 5 show that the epoxide characteristic peak at 834 cm^{-1} diminishes with the increase of TOFA/epoxide equivalent ratio. When the ratio TOFA/epoxide was 0.6:1, the peak at 834 cm^{-1} almost disappeared, and consequently there were OH characteristic peaks at 3300 cm^{-1}.

For the ring opening reaction, many catalysts can be selected, such as metal chelate,[9,10] imidazole derivatives, tertiary amine, phosphorus compound, and onium salt.[11] *Table* 4 shows the effect of various catalysts on ESO polyol preparation. No matter which catalyst was used, the reaction time needed to reach the specified final acid value

Table 4—Effect of Catalyst on ESO Polyol Preparation

Catalyst	TPP		ETPPB		TPP+DMFa	
Level (%)	Time (hr)	Acid Value	Time (hr)	Acid Value	Time (hr)	Acid Value
0.15	10	6.33	3.0	5.51	—	—
0.3	—	—	2.5	1.76	—	—
0.5	8	6.93	2.0	4.45	—	—
1	6	6.70	1.5	1.86	6.5	6.92

(a) TPP is 0.15%wt, DMF is 0.85% wt based on all reactants.

would decrease with the increase of catalyst amount. The addition of DMF solvent shortened the reaction time without changing TPP amount, but led to dark red/brown polyol. This may be due to unwanted oxidation or condensation reaction of substituted pyrrole compounds.[12]

As shown in *Table* 4, ETPPB appeared to be a more effective catalyst than TPP in ESO polyol preparation. At the same catalyst level, 0.15% wt based on all reactants, ETPPB can shorten reaction time from 10 to three hours.

Urethane Prepolymer Preparation

The moisture curable resin can be prepared by reacting an appropriate polyol with various di- or triisocyanates followed by end capping as shown in *Figure* 6.

The prepolymers listed in *Table* 5 were prepared from the ESO polyols catalyzed by TPP and MDI using DBTDL as the urethane catalyst. We used the equivalent ratio of isocyanate to polyol=1.5:1 only for the system where the fn of polyol were no more than 2 (Polyol A and B, see *Table* 3).

Generally, in order for the reaction to proceed without gelation, the concentration of resin should be kept around 50% w/w. The best reactions were those in which the NCO/OH ratio was around 2.0 which also resulted in the residual %NCO of 1.1-1.79. We attempted to prevent the premature gelation from occurring by reducing the reaction time and temperature, but it resulted in higher residual NCO content (lower reaction conversion). This, in turn, necessitated the addition of more silane in the end-capping reaction, where again gelation happened. By decreasing the reactant concentration to or below 50%, stable urethane prepolymer solution can be obtained. This can be attributed to the very limited formation of allophanate groups from the reaction of urethane group and isocyanate functionalities. It was also discovered that the presence of ETPPB (from polyol preparation reactions) eliminated the need for the use of DBTDL urethane catalyst.

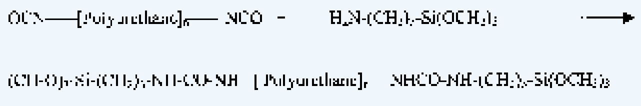

Figure 6—Schematic representation of a silane end-capped polyurethane.

Silane End-Capping Reactions

The stable urethane prepolymer solutions were then capped with amino silane at room temperature, which gave rise to the resin solution of moisture curable coatings. The reaction of soybean prepolymer with amino silane is fast and can take place at room temperature. The addition of a small amount of anhydrous methanol tends to stabilize the resin and prevents it from premature gelling upon storage. A schematic representation of silane end capping is shown in *Figure* 6.

The silane end-capped soybean polyurethane, after application and upon exposure to ambient moisture, hydrolyzes rapidly to silanol containing polyurethane compounds. The subsequent condensation produces a highly crosslinked matrix yielding a tack-free film in a short period of time depending on the temperature and relative humidity. A typical clearcoat formulation is shown is *Figure* 7.

Table 5—Effect of Some Parameters on Urethane Prepolymer Preparation

Polyol	Equivalent Ratio of NCO/Polyol	Concentration of Urethane Solution (%)	Reaction Stability	Residual NCO (%)
A	MDI:A=0.5:1	64	Good	0
	MDI:A=0.7:1	54	Good	0
	MDI:A=1.5:1	30	Good	0.53
	MDI:A=1.95:1	30	Good	1.10
B	MDI:B=1.5:1	55	Gel after 30 min	—
	MDI:B=1.95:1	60	Gel	—
	MDI:B=1.5:1	31	Good	0.66
	MDI:B=1.95:1	31	Good	1.32
C	MDI:C=1.95:1	30	Good	1.64
	MDI:D=2.0:1	40	Good	1.79
D	MDI:D=0.5:1	60	Good	0
	MDI:D=0.8:1	55	Gel	—

Material	Amounts
Moisture cure resin 45DL	78
Alkoxysilane	2
Acetone	7.85
Rheology control agent	7.8
Caster oil	2
Methanol	2
Titanium coupling agent	0.015
Defoamer	0.24
Surface active agent	0.1
Total	100.00

Figure 7—Prototype clearcoat formulation.

Gloss white moisture monocoat	
Solids % w/w	55.0
Application Visc. Sec. Z#2	60.0
P/B	0.42
VOC g/L (calculated)	350
Shelf life (months)	3-6
Hiding power (microns)	30.0
Tack-free time @ 25°C/50% RH (min)	25
Re-coat @ 25°C/50% RH (min)	60
Gloss 60°	96

Figure 8—Formulation characteristics.

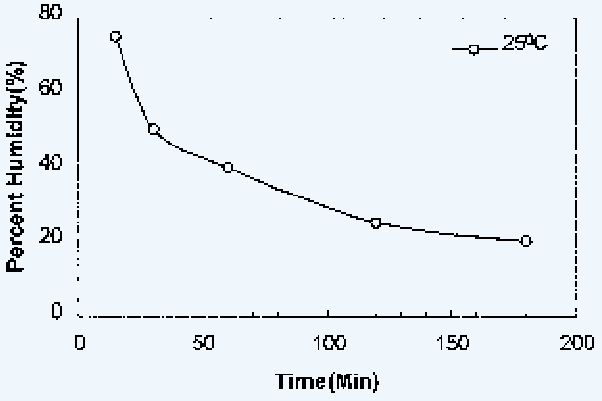

Figure 9—The humidity dependence of cure speed (surface dry) at constant temperature.

The formulation characteristics of a typical gloss white monocoat is shown in *Figure* 8.

Most clearcoat or pigmented coatings, depending on environmental temperature and humidity, become tack-free within 30-60 min after the application. Lower temperatures and humidity tend to extend the cure times. Since the cure is initiated by the formation of silanol moieties, the presence of a small amount of water in the form of environmental humidity is essential. The crosslinking reactions are considerably faster at elevated temperatures and high humidity such as 40°C/90% RH. At temperatures below 3°C and below 20% humidity, the cure reactions are very slow. The humidity dependence of the cure speed (surface dry or tack-free time) is shown in *Figure* 9. Unlike conventional isocyanate terminated moisture cure coatings, this system is only catalyzed (initiated) by the environmental moisture; therefore, its cure does not become impeded by the skin formation. However, a full cure and property development requires a seven-day aging. Some of the key coating properties are listed in *Table* 6.

CONCLUSIONS

Polyols derived from soybean oil and its derivatives were synthesized and characterized. The most useful polyols were those prepared through the ring opening mechanism using fatty acids. This method has not been reported in the literature and was discovered to be the most efficient and economical procedure of polyol production.

The polyols were used as the base resin for the preparation of isocyanate-free moisture cure resins. While the prepolymers can be used as coating raw materials for the conventional moisture cure system, they were further reacted with aminosilane coupling agents to afford isocyanate-free fast-curing resins. The silane end-capped resins can be stored for up to six months under anhydrous conditions. The resins were formulated as clearcoat and pigmented coatings. The prototype coating formulations produced coating films with excellent physical and chemical properties. Most clearcoat or pigmented coatings, depending on environmental temperature and humidity, become tack-free within 30-60 min after the application. Lower temperatures and humidity tend to extend the cure time. At temperatures below 5°C and below 25% humidity, the cure reactions are very slow. The cure rates of most moisture cure coatings were significantly better than the conventional alkyd coatings.

ACKNOWLEDGMENTS

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-Table 6—Key Properties of Moisture Cure Clearcoat

DFT	Tack-free Time	Re-coat Time	Full Cure[a]	Adhesion[b]	Impact D/R in.-lb	MEK Rub	Pencil Hardness	Flexibility 1/4 in.
45µ	30 min.	1 hr	48 hr	5B	120/100	>200	H	Pass
90µ	45 min.	1 hr	72 hr	5B	120/80	>200	H	Pass

(a) @ 25oC/50% RH.
(b) Substrates: Pressed wood, iron phosphated steel, cold rolled steel, masonry, oak veneer.

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