Novel Coatings From Soybean Oil Phosphate Ester Polyols

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Novel coatings with excellent properties have been formulated from polyols derived from the renewable resource soybean oil. Partially and fully epoxidized soybean oils (ESBO) were converted to novel soybean oil phosphate ester polyols (SOPEP) which were successfully incorporated into solventborne and waterborne bake coatings. Thermally cured waterborne alkyd coatings were produced with improved coating adhesion, low volatile organic compounds (VOC), excellent impact resistance, good hardness, less severe curing conditions, and lower cost. Solventborne alkyd coatings gave similar results. Soybean oil phosphate ester polyols appear to offer the coatings industry a low cost route to tough, durable, environmentally compliant, high performance coatings.

INTRODUCTION

Soybean oil (SBO) is the most readily available and one of the lowest-cost vegetable oils in the world.[1,2] It consists of triglycerides of a mixture of fatty acids formed by the reaction of glycerine and three fatty acid molecules. Epoxidized soybean oil (ESBO, *Figure* 1) is the result of the oxidation of soybean oil with hydrogen peroxide and either acetic or formic acid. According to the ratio of double bonds converted to epoxy groups, one can get partially epoxidized soybean oils such as 1/3, 1/2, 2/3 ESBO, and fully epoxidized 3/3 ESBO. Both soybean oil and ESBO are industrially available in large volume at low price. In recent years, there has been a decline in the coating market share of soybean oil alkyds due to growth of latex paints that have lower VOC, low odor, improved properties, and ease of cleanup. Most recently, the higher VOC of alkyds has been a major problem. Improvement in adhesion and corrosion resistance along with reduced VOC and reduced cost would make industrial alkyds more viable. Some envisioned soybean derivatives have the potential to improve adhesion, resist corrosion, and reduce VOCs and the cost of coatings.

In our group's earlier work, ESBO had been directly incorporated into air-dry alkyd systems as a reactive diluent[3] and in a cationic UV-cure system as an additional epoxy component.[4] There were adhesion problems in the UV-cured coatings with or without ESBO. In this work, the technology of epoxy phosphate esters was employed to reduce the VOCs of industrial bake coatings and improve adhesion. It was found before that the phosphate ester group made organic resins dispersible in water so one could produce waterborne alkyd coatings with lower VOC and excellent physical properties.[5-7] The phosphate ester group was also found to increase the adhesion to metal substrates by reaction with the metal, thus providing a strong chemical bond between the coating polymer and the metal.[8-10] This metal-phosphate bond is more resistant to displacement by water than the normal coating hydrogen bond to metal substrates and contributed to improvements in corrosion resistance of the coatings as well. This technology can be traced back to the late 1970s. Martin claimed water-thinnable epoxy phosphate esters

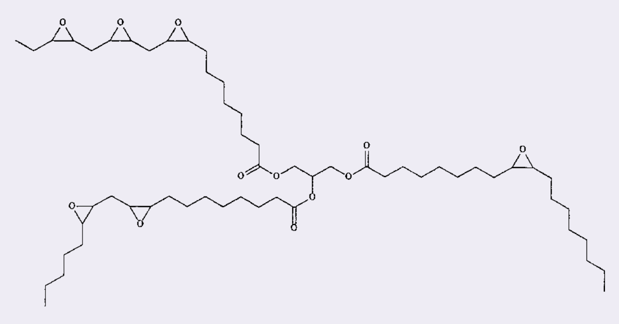

Figure 1—Epoxidized soybean oil .

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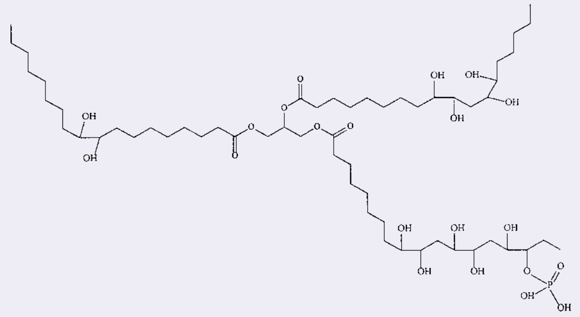

Figure 2—Soybean oil phosphate ester polyol (SOPEP).

and a process to make them in 1979.[11] Numerous patents modified the process or used the epoxy phosphate esters to modify coating properties.[12-16] Massingill extended the application of epoxy phosphate esters by teaching their use in solventborne coatings for improved adhesion and corrosion resistance.[17] These papers focused primarily on bisphenol-A epoxy resin formulations.

Novel soybean oil phosphate ester polyols (*Figure* 2) have been synthesized from partially and fully epoxidized soybean oils.[18] Processes have been developed in order to control oligomer formation and minimize hydrolysis of the glyceryl ester bonds in ESBO. The resulting phosphate ester polyols had several types of functional groups: polyols for hydroxyl-cure mechanisms, and the phosphate ester group for adhesion and water reducibility. They also had unsaturation for oxidative crosslinking. Our new processes cover a range of phosphate epoxy ratios and produce a phosphate ester polyol with very little free fatty acid. The results of formulation work showed that these polyols can be successfully incorporated into both solventborne and waterborne coating systems with equal or better overall coating performance. In addition, it can be used in UV-cure coatings that give good physical performance. Other societal benefits include less air pollution and less dependence on foreign oil.

EXPERIMENTAL

Materials

Three experimental types of ESBO—1/3 ESBO, 1/2 ESBO, and 2/3 ESBO—and a commercial, fully epoxidized ESBO or 3/3 ESBO (Vikoflex 7170, EEW 231) were kindly supplied by ATOFINA. Cellokyd™ 2849-X (a high-solids short oil TOFA alkyd) was supplied by Reichhold. Cymel™ 303, 323 (melamine/formaldehyde resins), and 4040 (acid catalyst) were supplied by Cytec. BYK™ 053, 301, and 361 are additives supplied by BYK-Chemie. Xylene, methyl ethyl ketone (MEK), N,N-dimethyl ethanol amine (DMEA), p-toluene sulfonic acid monohydrate (PTSA), and super phosphoric acid (105%) were supplied by Aldrich Chemical Co. Dowanol™ DB (Diethylene glycol butyl ether) and Dowanol EB (ethylene glycol butyl ether) were supplied by The Dow Chemical Company. Resydrol AY 586 W, supplied by Vianova Resins, is a commercial-grade waterborne alkyd resin based on core shell technology that is 38% in water containing 5.6% 2-butoxy ethanol (EB). The acid number of this resin is 61 mg KOH/g resin, and the hydroxyl value is 44 mg KOH/g resin. Polyol Tone™ 0301 (a caprolactone triol, OH# 95) was supplied by Union Carbide Corp. Iron phosphated steel panels (R-36-I) were supplied by Q-Panel Co.

Synthesis of Soybean Oil Phosphate Ester Polyol

All reactions were carried out in either a 250 or 500 ml four-necked flask equipped with a variable speed stirrer, a thermometer, a nitrogen inlet tube, a condenser and a dropping funnel. The flask was heated with an electric heating mantle connected to a variable voltage transformer. A thermo-watch L6-1000ss was used to control the temperature.

Phosphorylation

One hundred grams of epoxidized soybean oil was charged into the four-necked flask under agitation and kept at room temperature (25°C). Then 1 g (1% by weight based on oil) super phosphoric acid was dissolved in 10 g DB then added drop by drop into the oil. Since the reaction is exothermic, the temperature rose to 30-35°C. After adding all the mixture of super phosphoric acid and DB, stirring was continued for 30 min. The epoxy value was measured every 10 min, until the number was constant.

Hydrolysis

The phosphorylated resin was then heated to 110°C, and a mixture of water and a small amount of phosphoric acid was added drop by drop. After adding all the mixture, the temperature was held at 100-110°C. The epoxy value and acid number were measured every hour, until the epoxy value was almost zero. Then the resin was cooled and transferred to a sample container.

Solventborne Coatings

A commercial alkyd and starter coating formulation (*Table* 2) were employed to test the effect of SOPEP on coating properties. Based on this original recipe, the alkyd resin was replaced with SOPEP from 10-50%. After all the ingredients had been mixed, MEK was used to adjust the viscosity to about 300-400 mPs.

Waterborne Coatings

A quantity of SOPEP, Resydrol AY 586W, Cymel 323, BYK 301, and DMEA were charged to a can (200 ml) with stirring. The mixture turned to a white opaque liquid.

Table 1—Parameters of Epoxidized Soybean Oils

	1/3 ESBO	1/2 ESBO	2/3 ESBO	3/3 ESBO
Iodine value (IV)	90.35	71.80	45.55	1.35
Acid number (AV)	0.34	0.21	0.29	0.08
Oxirane percent	2.63%	3.49%	4.79%	6.91%
Measured E.V.[a]	0.16	0.21	0.30	0.42

(a)Epoxy value (E.V.) is the number of moles of epoxy groups per 100 g of resin.

Table 2—Formulations of SOPEP in Alkyd Coatings. 1:1 Alkyd:SOPEP Ratio

	Fs$_1$	Fs$_2$	Fs$_3$	Fs$_4$	Fs$_5$	Fs$_6$
Degree of Oil Epoxidation	—	1/3	1/2	2/3	3/3	3/3
Cellokyd 2849-X	24	12	12	12	12	—
SOPEP	—	12	12	12	12	24
Cymel 303	24	24	24	24	24	24
Cymel 4040	0.02	0.02	0.02	0.02	0.02	0.02
BYK 361	0.02	0.02	0.02	0.02	0.02	0.02
Xylene	5.0	3.0	3.6	4.4	5.0	5.0
MEK	2.0	2.0	2.0	2.0	2.0	2.0
Properties						
Viscosity (cPs)	380	340	358	372	392	406
NVW (%)	77	88	85	81	79	78
VOC (lb/gal)	2.03	1.68	1.73	1.80	1.87	1.84
Film thickness (mil)	1.0	1.0	1.1	1.2	1.1	1.0
Pencil hardness	4H	H	1~2H	2H	2~3H	B
MEK double rubs	>200	120	120	>200	>200	35
Adhesion	4B	4B	4~5B	5B	5B	3B
Impact resistance (D/R)	140/120	140/120	140/120	140/140	160/160	120/100

After five minutes mixing, distilled water was added slowly into the mixture. Stirring was continued for 30 min after all the water had been added. The color of the coatings changed from milky white to milky yellow. The resulting emulsion had a pH range of 8-9 and was about 55% nonvolatile weight (NVW). The pH was adjusted by addition of DMEA as needed.

Panel Preparation

Q-Steel panels (R-36) were wiped with MEK, and allowed to dry. The coatings were applied with a bird blade drawdown bar. Solventborne coatings were 2.0 mil wet film thickness and waterborne coatings were 0.6 mil wet film thickness. The coated panels were left at room temperature for 5-10 min before being placed in the oven to bake for 30 min. Solventborne coatings were baked at 145°C and waterborne coatings were baked at 150°C. After baking, panels were left at room temperature overnight before testing.

Characterization Methods

Acid number (A.N., ASTM D 1639), hydroxyl number (OH#, ASTM D 1957), epoxy value (E.V., ASTM D 1652), pencil hardness (ASTM D 3363-92a), cross-hatch adhesion (ASTM D 4752), solvent resistance (ASTM D 5402), impact resistance (ASTM D 2794-92), and non-volatile weight (ASTM D 2369) were determined. Viscosity was measured with a Brookfield viscometer at 25°C. Film thickness was measured by using a Microtest magnetic coating thickness gauge. Each panel had an average of three measurements to determine the thickness of the panels. Particle size of water-reducible coatings was measured with a laser diffraction instrument, Microtac Series 9200. The results were recorded as a volume distribution. The measurement process involved dilution of the emulsion with water to about 50:1. The particle size and distribution were the average results of the record in 180 sec for two times.

Table 3—Effect of Alkyd/SOPEP Ratio

	Fs$_8$	Fs$_9$	Fs$_{10}$	Fs$_{11}$	Fs$_{12}$
Formulation %SOPEP	—	10	30	50	70
Cellokyd 2849-X	24	21.6	16.8	12	7.2
3/3 SOPEP	—	2.4	7.2	12	16.8
Cymel 303	24	24	24	24	24
Cymel 4040	0.02	0.02	0.02	0.02	0.02
BYK 361	0.02	0.02	0.02	0.02	0.02
Xylene	5.0	5.0	5.0	5.0	5.0
MEK	2.0	2.0	2.0	2.0	2.0
Properties					
Viscosity (cPs)	380	378	383	387	373
NVW (%)	77	77	78	79	81
VOC (lb/gal)	2.03	1.97	1.90	1.87	1.84
Film thickness (mil)	1.0	1.0	1.1	1.1	1.1
Pencil hardness	4H	3~4H	3H	2~3H	HB
MEK double rubs	>200	>200	>200	>200	80
Adhesion	4B	4~5B	5B	5B	5B
Impact resistance (D/R)	140/120	140/140	160/160	160/160	120/120

RESULTS AND DISCUSSION

The parameters of the epoxidized oils used are given in *Table* 1. Oxirane content varied from a low of 2.6% to a high of 6.9%. All of the oils except the fully epoxidized oil were research samples produced for this project.

Solventborne Coating Systems

A commercial solventborne coating system was employed to test the properties of soybean oil phosphate ester polyol. The formulations and the resulting coating properties are shown in *Table* 2. Fs$_1$ was the formula recommended by the resin supplier. For formulas Fs$_2$-Fs$_5$, the ratio of Alkyd/SOPEP was 50/50 and the ratio of (Alkyd+SOPEP)/Cymel was 50/50. Fs$_1$ was cured at 175°C

Table 4—Effect of SOPEP/Alkyd Ratio on Waterborne Coatings

Formulation (g)	Fw_0	Fw_1	Fw_2	Fw_3	Fw_4	Fw_5	Fw_6	Fw_7
1/3 SOPEP/Resydrol	0:100	20:80	30:70	40:60	50:50	60:40	70:30	80:20
1/3 SOPEP	0	1.08	1.62	2.16	2.7	3.24	3.78	4.32
Resydrol AY 586W	6	4.8	4.2	3.6	3.0	2.4	1.8	1.2
Cymel 303	4	4	4	4	4	4	4	4
BYK 361	0.08	0.08	0.08	0.08	0.08	0.08	0.08	0.08
DMEA	0.26	0.28	0.29	0.30	0.31	0.33	0.34	0.35
PTSA	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Water	4	4	4	4	4	4	4	4
Coating Properties								
Film thickness (mil)	0.3	0.3	0.3	0.3	0.3	0.4	0.4	0.4
Pencil hardness	2H	2H	2H	2H	H	HB	B	2B
MEK double rubs	>200	>200	>200	>200	>200	>200	>200	>200
Adhesion	3B	5B	5B	5B	5B	5B	5B	5B
Impact resistance (D/R)	120/100	120/120	140/120	160/140	160/160	160/160	160/160	160/160
NVW (%)	40	44	47	55	59	58	57	55

Note: The ratio (by wt.) of (1/3 SOPEP + Resydrol)/Cymel 303 is 60:40.
Coatings on steel panels were baked 30 min at 275°F.

for 30 min while the bake temperature of the SOPEP formulations was reduced to 145°C for 30 min. Film appearance of all the coatings was smooth and glossy with no surface defects.

The results show that the 1/3, 1/2, 2/3 and 3/3 SOPEP can be successfully incorporated into alkyd coating systems at up to 50% of the resin. Generally, all the polyols tested can provide acceptable properties. With SOPEP as the only resin in the coating, we obtained a coating with medium properties, shown as Fs_6. We conclude the following from *Table* 2:

(1) SOPEP is a good, environmentally compliant co-resin, which can reduce the VOC of coatings. The SOPEP made from 1/3 epoxidized soybean oil gave the lowest VOC formulation.

(2) Adhesion was improved for 2/3 and 3/3 SOPEP formulations.

(3) Solvent resistance of the 1/3 and 1/2 SOPEP was good, but somewhat lower than the standard, while the 2/3 and 3/3 SOPEP had performance equal to the standard.

Table 5—Comparison of 1/3 and 1/2 SOPEP in Waterborne Coatings. 60:40 Alkyd:SOPEP Ratio

Formulation (g)^a	Fw_8	Fw_9
1/3 PO-SBO (PE)	2.4	—
1/2 PO-SBO (PE)	—	2.4
Resydrol	3.6	3.6
Cymel 323	4.0	4.0
BYK 361	0.08	0.08
DMEA	0.22	0.24
Water	2	2
Coating Properties		
Film thickness (mil)	0.3	0.3
Pencil hardness	H	2H
Adhesion	5B	5B
MEK double rubs	>200	>200
Impact resistance	140/140	80/80
Viscosity cPs (6 rpm @ 25°C)	269.9	439.9
NVW (%)	53	56

(a) The ratios (by weight) of the binder system: SOPEP/Resydrol = 40:60, (SOPEP + Resydrol)/Cymel 323 = 60:40.

(4) The 3/3 SOPEP formulation gave a coating with increased impact resistance.

(5) Hardness increased with increasing hydroxyl functionality. The polyol made from fully epoxidized soybean oil gave a pencil hardness slightly less than the standard.

(6) An unexpected effect of incorporation of SOPEP was the lower curing temperature needed, which may be due to the high functionality of SOPEP.

(7) Of the four types of SOPEP investigated, 3/3 SOPEP had the best overall properties and performance. In addition, 3/3 SOPEP gave excellent overbake resistance while the SOPEP with residual double bonds could overbake to give yellow coatings.

(8) A coating made of only SOPEP and crosslinker can give coatings with medium properties.

Since 3/3 SOPEP gave the best overall performance, we investigated it in formulations with different Alkyd/SOPEP ratios using from 10-70% SOPEP as the resin. The results in *Table* 3 show that 10-50% SOPEP in the alkyd coating was acceptable and could give lower VOC, better adhesion, and better impact resistance at some sacrifice of hardness. Even at a 30:70 Alkyd:SOPEP ratio, the resulting coating had good adhesion, modest MEK double rubs, and HB hardness.

Waterborne Coating Systems

A commercial waterborne alkyd resin was employed to investigate the properties of SOPEP in water-reducible coatings. The results in *Table* 4 show that 1/3 ESBO can be successfully used as co-resin in water-reducible alkyd coatings with good film properties. Adhesion was improved with addition of just 20% SOPEP. Solvent resistance was equal even at an Alkyd:SOPEP ratio of 20:80. Up to 40% SOPEP can be incorporated without sacrificing hardness while the impact resistance was improved with increasing the amount of SOPEP in the formulation.

Table 6—Effect of 40% SOPEP in Commercial Resin

Alkyd: SOPEP Ratio Coating Properties	100:0	60:40
Film thickness, mil	0.6	0.5
Adhesion	2B	5B
Pencil hardness	2H	2H
MEK double rubs	>200	>200
Impact resistance (D/R)	80/80	120/120

The effect of increasing the hydroxyl functionality is shown in *Table* 5. The extra hydroxyl functionality of 1/2 SOPEP gave a harder film with less flexibility; other film properties were equivalent.

A standard coating based on commercial waterborne alkyd resin AY586 was prepared and compared with a clear coating with 40% by weight incorporation of the phosphate ester polyol. A comparison of the film properties is shown in *Table* 6. The adhesion of the coating improved from 2B to 5B, hardness was not affected, solvent resistance was maintained, and impact resistance increased. The coating based on 40% polyol and 60% AY585 not only gave equal or better properties, it was stable for three weeks at 50°C.

CONCLUSIONS

Soybean oil phosphate ester polyols were synthesized successfully and incorporated in bake coatings with excellent results. The resins are low molecular weight for low viscosity and low VOC and highly functional for excellent crosslinking. The polyols have two useful functional groups: phosphate groups for adhesion improvement and water dispersion and glycol groups for crosslinking. Several of the SOPEP resins also had residual unsaturation for oxidative crosslinking.

All four types of SOPEP investigated can be incorporated into solventborne coatings with lower VOC, good adhesion, improved impact resistance, and lower curing temperature. Epoxidized soybean oil phosphate ester polyol from commercial fully epoxidized soybean oil gave the best overall properties and performance.

For water-reducible coatings, 1/3 and 1/2 SOPEP can be dispersed successfully in water to give very low VOC coatings with improved adhesion, improved impact resistance, and equivalent pencil hardness and solvent resistance.

Soybean oil phosphate ester polyols potentially offer the coatings industry a low cost route to tough, durable, environmentally compliant, high performance coatings.

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