

PROJECT SUMMARY- California Air Resources Board ICAT Grant No. 02-02

High Performance Low VOC Coatings for 2006

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This project was a collaborative effort to produce prototype high performance drum and wood coatings with a target of 100 g/L VOC or less from new hyperbranched vegetable oil polyol phosphate esters (POLYOL) and give a commercial application demonstration that compares the prototype paints with existing paints for VOC and performance. POLYOL can be used as a waterborne short oil alkyd type resin or as a reactive co-resin with short oil alkyds and polyester resins for metal bake coatings with good adhesion and low VOC. It can also be used in ambient cure polyurethane coatings for wood.

Texas State University developed hyperbranched high performance phosphate ester polyol resin technology for reducing VOC in alkyd and other coatings to meet 2006 limits. The innovative aspect of the new resins is their hyperbranched technology combined with water dispersibility and corrosion resistance via the phosphate ester groups. It is innovative in that the hyperbranched resins give similar performance to current commercial linear resins at one-tenth the viscosity by reducing polymer chain entanglement. This innovation is important in that it allows waterborne and solvent based alkyd paints to achieve conventional performance at unconventionally low VOC. The unconventional use of the phosphate ester for dispersion reduces the need for surfactant and the phosphate dispersing group reacts with metal substrates to improve adhesion and improve corrosion resistance of the coating.

The bio-based hyperbranched alkyd technology should, at high production volume, provide lower cost, equivalent performance, and lower VOC than is provided by commercially available alkyd technology. The new waterborne technology has the capability of producing high performance short oil alkyd-type paints that are compliant with projected emission standards for 2006. It performed in the ICAT funded demonstration project as expected and met performance requirements at VOCs of 100 g/L and less using commercially available ingredients.

Arkema is developing POLYOL to become a commercial product. In 2002 the cost of the new soybean oil phosphate ester polyol was projected to be about \$0.70/lb at high volume production. Alkyd resin costs at that time varied from about \$0.75-2.00/lb. A February 2005 commercial quote for the soy polyol in bulk was \$1.50/lb. This price was a major disappointment. Valspar was evaluating the product for cost savings in wood coatings based on the projected price of around \$0.70/lb, but ceased work when the price of \$1.50 was quoted them. Precision Coatings continued to work with the soy polyol because of its low VOC potential. Soy polyol is made by addition of water and phosphoric acid to epoxidized soybean oil.

Short oil alkyd bake resins and long oil ambient cure resins were prepared and evaluated. Collaborators were Arkema, Precision Coatings, Dunn-Edwards, National Ink, Niemann & Associates, Valspar, Cook Composites and Polymers, Sherwin-Williams, and Rohm & Haas.

Precision Coatings qualified lab prepared POLYOL3.5 from Texas State and from Arkema. Precision Coatings then qualified a 10 gallon pilot scale preparation of POLYOL3.5 from Arkema. Precision Coatings then conducted a Demonstration of the new 174 g/L low VOC POLYOL based black container coating on April 11, 2006 at a Customer Plant in the South Coast Air Quality Management District. Five gallons of black POLYOL formulation were used to purge the paint lines and spray paint three drums on the commercial line. The three drums were flash dried, baked, cooled, and removed from the line for visual inspection and testing. Bill Murray commented that the coatings had good flow, good gloss, good adhesion, and good MEK solvent resistance. The drums had some streaking, possibly due to inadequate wetting. This occurred last year on plant start-up with the regular coatings and was corrected by reformulation. Precision Coatings intends to commercialize the coatings.



The following presentations on POLYOL preparation and use in short oil alkyd coatings and in polyurethane coatings for wood were made:

1. Vijay M Mannari and John L Massingill, Jr., “**Hyperbranched Soy Alkyd Resins For Low Voc Industrial Coatings**”, Proceedings of the 29th International Waterborne, High-Solids, & Powder Coatings Symp., New Orleans, Feb. 2002.
2. Vijay M Mannari and John L Massingill, Jr., “**Two-Component High-Solids Polyurethane Coating Systems Based On ‘Soy-Polyol’**”, Proceedings of the 29th International Waterborne, High-Solids, & Powder Coatings Symp., New Orleans, Feb. 2002.
3. “**Bio-Based Hyperbranched Polyols and Polymers**”, PMSE Division, National Meeting of the Amer. Chem. Soc., April, 2002.
4. V. M. Mannari, Y. Guo, Z. Chen, and J. L. Massingill, Jr., “**Epoxy Acid Phosphate Esters- Dispersibility And Salt Fog Resistance**”, Proceedings of the 30th International Waterborne, High-Solids, & Powder Coatings Symp., New Orleans, Feb. 2003.
5. Vijaykumar Mannari, Yinzhong Guo, and John L. Massingill, Jr., “**Dispersibility of phosphated bio-based hyperbranched polyols**”, 225th ACS National Meeting, Polymer Division, New Orleans, LA, March 2003.
6. A. Iyer, J. Massingill, “**Soy-Oil Based Tackifiers and Adhesives**”, 96th AOCS Annual Meeting, Salt Lake City, UT, May, 2005.

The following paper has been published:

Vijay M. Mannari and John L. Massingill, Jr., “**Two-Component High-Solid Polyurethane Coating Systems Based on Soy Polyols**”, JCT Research, *April 2006*.

The following papers have been written/submitted for publication:

1. Yinzhong Guo, Vijay M. Mannari, Pulin Patel, and John L. Massingill Jr., “**Self-Emulsifiable Soybean Oil Phosphate Ester Polyols for Low VOC Corrosion Resistant Coatings**”, submitted JCT Research.
2. A paper entitled “**Hydrolysis of Epoxidized Soybean Oil**” is being revised for submission to the Journal of the American Oil Chemists Society.

FINAL REPORT

Technology & Innovation:

Texas State (TXSTATE) developed hyperbranched high performance phosphate ester polyol resin technology for reducing VOC in alkyd and other coatings to meet 2006 limits. The resins are based on vegetable oil phosphate ester polyol (POLYOL).

The innovative aspect of the new resins is their hyperbranched technology combined with water dispersibility via the phosphate ester groups. It is innovative in that the hyperbranched resins give similar performance to current commercial linear resins at one-tenth the viscosity by reducing polymer chain entanglement. This innovation is important in that it allows waterborne and solvent based alkyd paints to achieve conventional performance at unconventionally low VOC. The unconventional use of the phosphate ester for dispersion reduces the need for surfactant and the phosphate dispersing group reacts with metal substrates to improve adhesion and reduce the water sensitivity of the coating.

With the bio-based hyperbranched alkyd technology, the TXSTATE technology provides lower cost, equivalent performance, and lower VOC than is provided by commercially available alkyd technology. The new waterborne technology has the capability of producing high performance paints that are compliant with projected emission standards for 2006. It should perform in the ICAT project as expected because prototype paints have met performance requirements at VOCs of 100 g/L and less using commercially available ingredients.

The cost of the new soybean oil phosphate ester polyol was projected to be \$0.70/lb at the beginning of the project. Alkyd resin cost at the time varied from about \$0.75-2.00/lb.

Emission Benefit in California:

The TXSTATE innovation provides a new emission-prevention technology for coatings-waterborne hyperbranched resins. Alkyd bake coatings in 2002 had a permitted VOC of 275-420 g/L. Table 1 shows the 2002 VOC limits for various categories of coatings, followed by 2005 limits, and target VOCs for coatings using the hyperbranched POLYOL.

The VOC of alkyd bake coatings will be reduced to 100 g/L, for a reduction of 60-80%. The typical alkyd paint solvent is mineral spirits. We will reduce solvent demand by using low viscosity hyperbranched resins in waterborne formulations and use of hyperbranched resins with solvents of low atmospheric reactivity in solvent borne coatings.

Table 2 shows the volume for five targeted categories of paints in which POLYOL can be used and the potential VOC savings. If California paint volume is 10% of the US paint volume then the five paint categories released approximately 164,000 tons of VOC per year in California in 1995. The substitution of POLYOL in these paints could yield a potential VOC reduction of 66,000 tons of VOC per year in California if 50% market penetration can be achieved. The 2002 California Emissions Inventory indicated that 116,000 tons/yr of VOC were emitted from all coatings and inks. These numbers appear to be out of sync by about 30%. POLYOL could be used with 40% of the paint resins reported consumed in Europe in 1996. A similar ratio in California would

imply that only about 23,000 tons/year of solvent could be eliminated by the use of POLYOL at 50% market penetration. If POLYOL reaches 10% of the potential market it could prevent the release of approximately 4300 tons/year of VOC into California air.

Table 1. VOC Targets by Product Area Using POLYOL

Product	2002 AQMD VOC limit, g/L	2005 AQMD VOC limit, g/L	POLYOL VOC target g/L
Metal Containers			
Drums, new exterior	340		100
Drums, reconditioned, exterior	420		100
Cans, two piece, exterior	250		100
Cans, three piece, exterior	225		100
Coil	200		100
Metal Parts	275		100
Wood, flat stock	250		100
Wood products	550	275/120	100
Auto Refinish			
primer/surfacers	250		100
primer sealer	340		100
topcoat	420		100
Magnet Wire	200	150	100
Chemical Tank Coatings		100	
Floor Coatings	100	50	
Industrial Maintenance	250	100	100
Lacquer	550	275	
Quick Dry Enamels	250	50	

Table 2. Potential Effect of POLYOL Use in Paints

Product Line	Paint Volume* MM Liters	VOC** MM Kg/yr	VOC Prevented*** MM Kg/yr
Can & Coil	30	10.2	8.16
Wood	23	12.6	10.1
Auto Refinish	13	7.1	5.7
Metal Parts	21	5.8	4.6
Magnet Wire	2	.4	0.3
SUM	89	36.1 (164,000 ton/yr)	14.5 (66,000 ton/yr)

* Based on CA being 10% of 1995 US Volume ** Based on average CA VOC limit

*** Assume 80% VOC savings, 50% market penetration

The partial replacement of resins cured through their hydroxyl groups with hyperbranched POLYOL should be applicable to all bake coatings, many force dry coatings, many radiation cured coatings, and some ambient cured coatings. The actual replacement percentage achieved in practice will be limited by performance, price, and compatibility.

Commercialization/Business Plan:

1. Texas State University is an academic institution. TXSTATE will benefit by financial support of its staff and students by the project. TXSTATE will also benefit by the development of a network of potential funders for new and derivative projects. The PI, Dr. John Massingill, had 25 years of experience with The Dow Chemical Company in new product and process development. Millions of pounds per year of resins are produced each year around the world by processes he developed. Dr. Massingill was in Technical Service and Development for 9 years developing and introducing new resins to the paint industry.

B. Arkema is a major international chemical company fully capable with demonstrated experience in bringing new products to market.

C. Precision Coatings is a manufacturer of container coatings in Southern California.

D. Precision Coatings has contacts to toll manufacture POLYOL in California.

2. POLYOL is a new product combining the low cost advantages of vegetable oils and high tech hyperbranched technology for high performance. Paints made from POLYOL will be lower in cost to manufacture, have similar performance to current technology, and have lower VOCs.

In earlier work by the Principal Investigator at The Dow Chemical Company, the technology of epoxy phosphate esters was employed to reduce the VOCs of industrial bake coatings and improve adhesion and formability. It had been found earlier that the phosphate ester group made organic resins dispersible in water so one could produce waterborne coatings with lower VOC and excellent physical properties.^{1,2,3} 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.^{4,5,6} 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 late 1970's. Martin claimed water thinnable epoxy phosphate esters and a process to make them in 1979.⁷ Numerous patents modified the process or used the epoxy phosphate esters to modify coating properties.^{8,9,10,11,12} Massingill extended the application of

¹ P. Winner, et al. U.S. Pat. No. 4,487,861, 1984.

² Y. Yabu, U.S. Pat. No. 5,389,704, 1995.

³ R. G. Mysliwcyk, et al. U.S. Pat. No. 5,264,469, 1993.

⁴ J. L. Massingill, "Adhesion and Flexibility Contributions to the Performance of Epoxy Phosphate Ester Coatings", **J. Coat. Tech.** 63(797), 47-54, 1991.

⁵ J. L. Massingill and R. C. Whiteside Jr., "Formability Improvement of Epoxy Can & Coil Coatings, Blends of Epoxy Phosphate Esters", **J. Coat. Tech.**, 65(824), 65-71, 1993.

⁶ J. L. Massingill and D. Morisse-Arnold, "Properties of Solvent-Borne Epoxy Phosphate Ester Coatings", Proceedings 15th Intl. Conference in Organic Coatings Science and Technology, 1989.

⁷ P. H. Martin, U.S. Pat. No. 4,164,487, 1979.

⁸ D. R. Perine, et al U.S. Pat. No. 4,316,922, 1982.

⁹ K. D. Campbell, et al. U.S. Pat. No. 4,397,970, 1983.

¹⁰ K. Sekmaks, et al. U.S. Pat. No. 4,425,451, 1984.

epoxy phosphate esters by teaching their use in solvent-borne coatings for improved adhesion and corrosion resistance.¹³ These patents focused primarily on bisphenol A epoxy resin formulations, but taught the use of the epoxidized soy product. The basic vegetable oil phosphate ester polyol technology patent by The Dow Chemical Company has expired. Patents on derivatives and formulation compositions of matter could still be possible. Other applications of POLYOL include the UV cationic epoxy coating market, 54,000 metric tons in 1996 and growing at 10% per year. A cost reduction of 20-50% should accelerate the growth of this UV market. A 20% market share would equal 5 million pounds. Potential spin-off technologies include textile coatings and fire retardant textile coatings.

3. This new hyperbranched resin technology will be applicable to all categories of thermosetting paints and coatings that cure through hydroxyls. Solvent borne coatings should be able to reduce VOC by 25% (without exempt solvents) without impairing paint performance. The use of proposed exempt solvent t-butyl acetate should allow reduction in VOC of another 25-50%. If t-butyl acetate is exempted, solvent borne paints that meet 2006 proposed VOC rules are possible. Use of the water dispersible, low Tg, thermosetting POLYOL appears to be capable of producing waterborne paints that will meet 2006 emission regulations without sacrificing performance or increasing raw material costs.

4. Market Analysis- Original equipment manufacturers (OEM) usually decorate and protect their metal and wood products with special purpose paint. NIST estimates that 4.6% of the U.S. gross national product is lost to corrosion even with all the paints that we use to protect metal and wood. Coatings are crucial to the welfare of the U.S. infrastructure.

The OEM Coatings Market consumes \$5.4 Billion/year worldwide. In the U.S., the OEM market is 30% of all paint distributed by types as follows:¹⁴ The U.S., Europe, and the rest of the world have approximately equal shares of the world market for paint.

	<u>1992</u>	<u>1996</u>	<u>2004</u>
conventional low solids	68%	56%	51%
waterborne	7	12	17
high solids	21	25	23
powder	3	5	8
UV	1	1	3

This hyperbranched polyol technology will help increase the growth rate of waterborne, high solids, and UV cured coatings because it 1) reduces VOC, 2) reduces cost, 3) improves adhesion, 4) improves corrosion resistance, 5) improves flexibility, 6) improves durability, 7) maintains reasonable hardness, and 8) maintains high gloss and ease of application of alkyd coatings. POLYOL could have one million pounds in sales in the first year of commercial bulk production. POLYOL sales could accelerate at 50% per year as the low cost, low VOC, and high performance

¹¹ R. M. Christenson, et al. U.S. Pat. No. 4,638,020, 1987

¹² J. L. Massingill, et al. U.S. Pat. No. 4,820,784, 1988.

¹³ J. L. Massingill, U.S. Pat. No. 5,086,094, 1992.

¹⁴ John Bell, Coatings World May 2000.

coatings prove themselves in the marketplace. A 25% share of the 22 million pound short oil alkyd resin market is possible. More performance data is needed to estimate its use in polyester and polyurethane coatings and polymers.

The technical barriers to this new technology appear to be relatively small and manageable.

- a) We worked with Arkema to convert the hydrolysis process from 2-liter glassware to 10-gallon steel reactors and then to larger commercial production. This process chemistry is relatively straightforward and should present no difficulties in scale up. In fact, there is reason to believe that a process being developed by the P.I. can be developed that will produce POLYOL in less time with less side reactions than now occur.
- b) Coating performance in the real world has been demonstrated by Precision Coatings.

Other technical problems that need to be addressed in order to maximize market penetration are:

- 1) POLYOL is currently incompatible with some resins and curing agents. This can probably be fixed by simple modifications to POLYOL.
- 2) POLYOL coatings are currently slightly softer than current coatings, i.e., 4H vs. 3H or 2H. This can be adjusted as necessary by POLYOL modifications.
- 3) Arkema's lack of knowledge of the paint industry can be remedied by the Cook Composites and Polymers (CCP). CCP could work with Arkema for distribution of POLYOL to the paint industry, since they are both in the Total group (a French petrochemical giant)
- 4) Addition of water to a TSCA registered polymer generally does not create the need for another TSCA registration. POLYOL may be exempt from TSCA registration under this interpretation, or may be grandfathered by Dow Chemical registration of POLYOL at the initiation of TSCA. A PMN will require at least 6 months.
- 5) The Not Invented Here syndrome can best be overcome by clear demonstration of economic and performance benefits.
- 6) Vegetable oils have a reputation of variability because of changes due to geography and weather variations from year to year. POLYOL is a highly functional polyol and changes in the vegetable oils do not appear to be a significant problem. We used 1/3, 1/2, 2/3, and fully epoxidized soybean oil to demonstrate that useful coatings could be made with a wide fluctuation in hydroxyl content.

5. Competition- Products to improve alkyd bake coating performance and reduce VOC include core-shell technology by Vianova Resins (\$2.00/lb); hyperbranched polyols by Perstorp (\$3.00/lb); and acrylic polyacid based alkyd. The first two products should be much more costly than the soy hyperbranched POLYOL (\$0.70 in bulk). The technology in this project should reduce costs below that of current technology. The acrylic polyacid alkyd technology is developmental and is aimed at the architectural market.

POLYOL is compatible with Vianova core-shell technology and could reduce the cost of the binder by about 50% with equivalent properties.

6. Financial History of Funding- The United Soybean Board (USB) committed \$148,000 to the POLYOL pilot process, prototype preparation/evaluation, application demonstration, and market

expansion. The Iowa Soybean Promotion Board funded \$67,000 to high phosphate POLYOL for use in inks. The National Academy of Science funded \$84,000 for POLYOL derivatives for waterproofing. The USB matched the NAS with \$50,000. The USB also funded \$112,000 for POLYOL derivatives in adhesives. ARB funds were not used for the research. TXSTATE provided \$44,000 matching funds. A total of approximately \$505,000 for soy phosphate ester polyol research.

The Arkema contribution was in-kind commitments of 1/2 man-year per year for pilot plant operations and 1/4 man-year per year for technical service operations. This was worth approximately \$120,000/year for 3 years or about \$360,000.

Cook Composites, and Coatings, Precision Coatings, Sherwin Williams, Rohm & Haas, and Valspar contributed additional in-kind funds to evaluate/demonstrate/apply the polyol in paints and resins.

ARB provided \$99,324 specific funding for further POLYOL process/prototype work, hyperbranched alkyd prototype development, DEMONSTRATION PROJECT, and technology transfer to industry. The ARB funds provided financing to get prototype paints made and applications demonstrated in drum coatings and architectural coatings.

We expect the industry to start adopting POLYOL as soon as it is produced commercially in bulk quantities. Arkema developed a commercial plan and pricing structure in 2005 for developmental quantities. Vegetable oils have a range of prices depending on crop yields throughout the world in a given year. Blends of oils could be used to make POLYOL. New processes are being developed for epoxidation of vegetable oils.¹⁵ A new process for producing polyols from vegetable oils might be adaptable to produce POLYOL inexpensively.¹⁶ This process simply adds water to the peracetic acid epoxidation process. Perhaps it would also accommodate addition of H₃PO₄. As mentioned earlier, the P.I. is developing a new process for two phase organic reactions that could potentially provide an inexpensive route to POLYOL.

Since POLYOL can be made from inexpensive epoxidized vegetable oils in commercial equipment with no special modification, it could end up being made economically by four different categories of producers because the patent on POLYOL has expired:

- Epoxidized vegetable oil producers would potentially have the least expensive product.
- Resin producers could make it in the same reactor that they use to make resins and would save transfer costs. Also, they could tailor POLYOL phosphate ester content for proprietary products.
- Large paint companies with their own reactors could produce POLYOL and formulate to the paint in the same reactor for some cost savings.
- Small paint companies could find local toll producers that would produce POLYOL for them inexpensively.

¹⁵ Mizuno, Noritaka; Yamaguchi, Kazuya, "Polyoxometalate catalysts : toward the development of green H₂O₂ - based epoxidation systems", Chemical Record (2006), 6(1), 12-22.

¹⁶ Casper, David M.; Newbold, Trevor, "Method of preparing a hydroxy-functional vegetable oil ester useful as a monomer for the preparation of polyurethanes", U.S. Pat. Appl. Publ. (2006), 2006041156.

Pilot plant introductory (drum) quantities of POLYOL were projected to be available within the first year. However, drum quantities were not available when requested by Niemann & Associates and by Valspar. Conversion costs for POLYOL are minimal from the epoxidized oil. Production can be achieved in basic batch reactors or, most efficiently, from continuous dedicated reactors. Many batch chemical reactors are available for tolling production in the initial phases (1 MM lb/yr) before dedicated equipment is constructed. Maximum economic benefits of POLYOL will be realized from continuous dedicated reactors of >10 MM lb/yr. Normally this would require new capital, however, if the process in reference 16 is adaptable to the current process, new capital may not be required. Breakeven production via toll production using another company's excess capacity can be at a very low level, perhaps as low as 100,000 pounds. Real costs for marketing, distribution, and profit would raise the actual cost for sale for this low level of production.

Most resin producers and the larger paint companies could make their own POLYOL from the epoxidized oil. The manufacturers of epoxidized oil would make a profit on this option also. All three epoxidized oil manufacturers' production would be needed for the expected volume of additional sales of epoxidized oil envisioned for a successful POLYOL.

Marketing plan for POLYOL. Literature on the cost benefits and performance of POLYOL in container coating applications will be generated by Precision Coatings and given to their customers and potential customers. Samples of POLYOL are available on request in quart, gallon, and 5-gallon quantities to support demonstration and commercialization efforts of resin manufacturers and paint companies. Toll manufacturers can make POLYOL from the published procedures.

Ability to market POLYOL and derivatives. Arkema and Cook Composites & Polymers (both part of TOTAL) have the capability to make and market POLYOL and derivatives. Paint companies have the capability of marketing the paints and have toll manufacturers make POLYOL from published procedures.

7. Key Players- Arkema is one of the three major manufacturers of epoxidized oils. They supplied pilot plant development personnel and equipment to produce 10 gallon reactor quantities of POLYOL for industry evaluation. They will also supply technical service/marketing personnel to introduce the product to market and follow-up on the industry evaluations. TXSTATE supplied much of the initial contacts with technical leadership at resin and paint manufacturers- this was paid from project funds. Precision Coatings will produce the paint for the commercial demonstration in container coatings.

The Precision Coatings contact is Bill Murray. He has container coating business and was willing to use POLYOL in a demonstration project after he saw the TxState data for low VOC alkyd bake coatings.

Arkema has pilot plant facilities from one gallon to 100 gallon at their location in Bloomington Prairie, Minnesota. They provided process research, pilot plant scale-up, and are willing to supply technical service & marketing as the product grows. They have quoted a price of \$1.50/lb for POLYOL.

8. The commercialization of POLYOL will have economic benefits for California:
- Paints will be formulated and sold by California companies using the hyperbranched POLYOL
 - End users in California will apply the paints to products.
 - Meeting VOC regulations will allow paint manufacturers and applicators to continue operations in California.
 - All unsaturated oils can be epoxidized and converted to POLYOL with various levels of hydroxy content. Farmers that produce crops with unsaturated oils will find that there will be increased demand for use of their crops in industrial uses (up to 220 MM bushels). Vegetable oils derived from California crops such as corn oil and olive oil; or from potential crops such as Raphanus sativus (wild or oilseed radish- a potential herb as well as ground cover for the almond crop) and canola/rapeseed (being researched as potential crops for California) are potential feedstock for making POLYOL.
 - Processors that make plant oils will have increased demand for their oils (up to 2.2 Billion lbs of oils).
 - Chemical, resin, and paint companies that produce the polyol will find use for their products.
 - Paint companies will be able to formulate environmentally compliant paints with good long-term performance and excellent raw material cost savings (20 to 50%) generating higher profits and increased tax revenue.
 - Consumers will have good products and better air quality at a reasonable cost.
 - CARB will have helped reduce VOC in commercial alkyd bake coatings in California by approximately 60-95%.

Job Growth Potential

California paint companies involved in this project include Precision Coatings (El Monte) and Dunn-Edwards (Monrovia). We expect other paint companies to be interested in technology that allows VOC reduction without impairing paint properties. A small, innovative company like Precision Coatings could easily see significant growth by taking advantage of this technology rapidly. Precision Coatings is considering toll manufacture of POLYOL in California. Epoxidized soybean oil is available from U.S. and foreign sources, with a price range of \$0.42 (bulk)-\$1.25 (distributors) quoted on the internet. California paint companies would maintain business by economically meeting VOC limits while providing a quality product. There are alternative ways to produce consumer items that do not require paint, and other areas with less stringent VOC rules.

Benefits to ARB's Program

The mission of ARB is to promote and protect public health, welfare and ecological resources through the effective and efficient reduction of air pollutants while recognizing and considering the effects on the economy of the state. The use of hyperbranched technology in paints will allow the paint industry in California to meet performance requirements while reducing pollution and maintaining production in California.

This project will allow ARB to encourage the development and demonstration of improved, cost-effective clean air technologies. The project will provide an innovative way to combine a high performance OEM bake coating with low VOC to attain air quality standards and reduce public exposure to air toxics. This innovative clean air technology will be more economical because it is based on Sustainable Chemistry using renewable resources- vegetable oils- instead of petroleum. This project allows ARB to join a partnership of academia, farmers, resin manufacturers, and paint companies to reach a common goal. The results of this project will help ARB provide scientific and technical information necessary to design and implement the Board's programs and achieve 2006 VOC targets in waterborne and solvent borne paint formulations for drum and wood coatings.

Some major goals of the Board and the impact of this new technology for paints on those goals are as follows:

- Provide Safe, Clean Air to All Californians
 - Hyperbranched resin technology in paints has the potential to reduce VOC emitted into the atmosphere by approximately 23,000 tons/yr
- Protect the Public from Exposure to Toxic Air Contaminants
 - Hyperbranched resin technology in paints has the potential to also reduce HAPs.
- Provide Innovative Approaches for Complying with Air Pollution Rules and Regulations
 - Support of this innovative technology will provide a mechanism for paint manufacturers to comply with air pollution rules and regulations while producing quality products demanded by consumers.
- Base Decisions on Best Possible Scientific and Economic Information
 - This project will provide scientific and economic information on which 2006 rules can be based on.

Project

The project demonstrated paint that meets 2006 VOC proposed rules for OEM metal coatings in head-to-head comparison with current commercial paints. The demonstration paint used innovative waterborne hyperbranched polyols based on inexpensive vegetable oils. The prototype paint for container coatings from TXSTATE was formulated and modified by Precision Coatings in El Monte, CA and the performance of the paint demonstrated at a Precision Coating's customer location in the South Coast Air Quality Management District. This successful demonstration for container coatings opens the door to application for other container, coil, metal parts, auto refinish, and magnet wire coatings.

Formulation properties, formulation VOC, formulation curing properties, and coating physical properties were measured. A direct comparison for all of these factors will be made with current commercial paint. The tasks and initial milestones for the collaborative project and ICAT support are summarized below:

Table 3. Proposed Tasks and Milestones

	Task	Milestone	By	Time	ICAT Support
1	Optimize process	Low viscosity POLYOL	TXSTATE	1 st Qtr	no
2	Sampling List	Agree to test	TXSTATE	1 st Qtr	no
3	Contact Tech Directors	Sample/test schedule	TXSTATE	1 st Qtr	partial
4	Modify POLYOL	Compatibility, low temp cure	TXSTATE	2 nd Qtr	partial
5	10 gal pilot reactor	Gallons of POLYOL	Arkema	2 nd Qtr	no
6	Verify quality performance	In spec POLYOL paint performance	TXSTATE	2 nd Qtr	partial
7	Prototype alkyd resin	Low viscosity high performance	TXSTATE	2 nd Qtr	yes
8	Prototype paint	Metal, wood	TXSTATE	3 rd Qtr	partial
9	100 gal reactor	Drums of POLYOL	Arkema	3 rd Qtr	no
10	Marketing package	Cost, selling price	Arkema	3 rd Qtr	no
11	Sample resin paint manufacturers	Commercial tests	Arkema	3 rd Qtr	no
12	Container Demonstration	In spec coating	Precision Coatings	4 th Qtr	no
13	Market follow-up	Determine interest/ volume	Arkema/TXSTATE	4 th Qtr	no
14	Develop spectrum of paint	Broad market	TXSTATE	4 th Qtr	no
15	Semi-commercial process	Prove process	Arkema	5 th Qtr	no
16	Promote POLYOL Data reduction	Tech meetings Final Report	TXSTATE	3 rd -8 th Qtr	partial

We have discovered outstanding properties and uses of hyperbranched vegetable oil phosphate ester polyol (POLYOL). Vegetable oil coatings are usually soft because of the low glass transition temperature of the fatty acids. We have made multifunctional hyperbranched polyols from vegetable oils and used them at high levels in paints that develop high Tg and perform very well in prototype coatings. The technology hydrolyzes commercial epoxidized vegetable oils with water and phosphoric acid to make POLYOL (Figure 2). Epoxidized soybean oil (ESO, Figure 1) is produced commercially as a plasticizer for PVC plastic. Capacity is about a160 MM lbs/yr.



Figure 1. Epoxidized Vegetable Oil

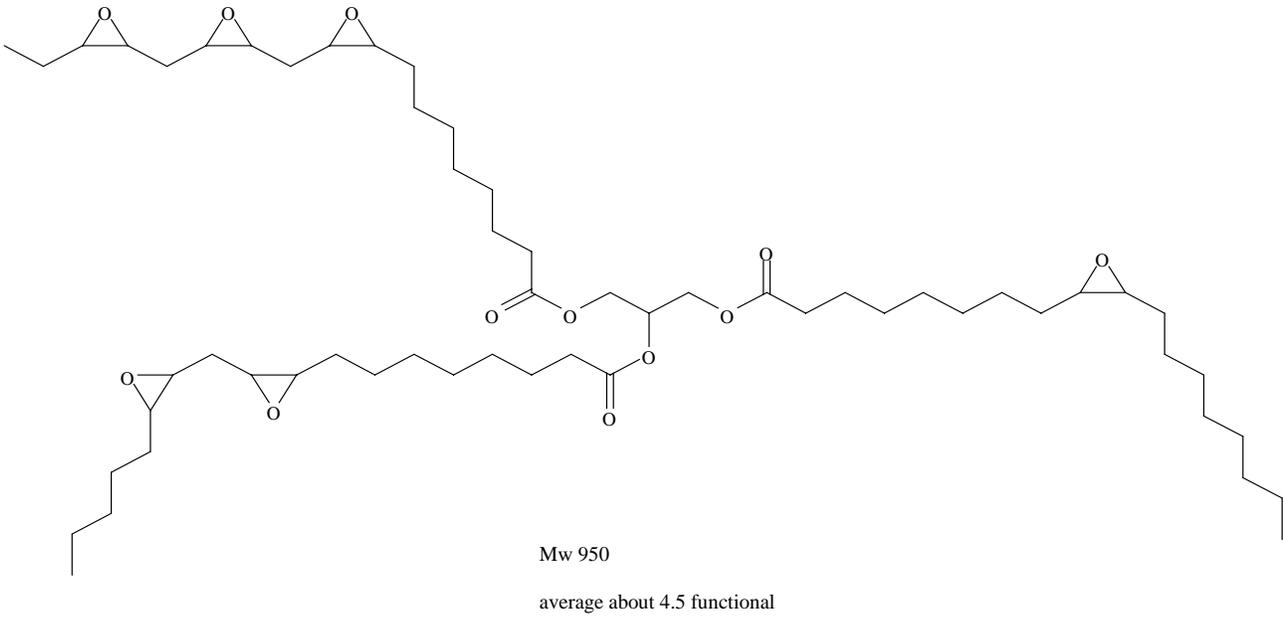
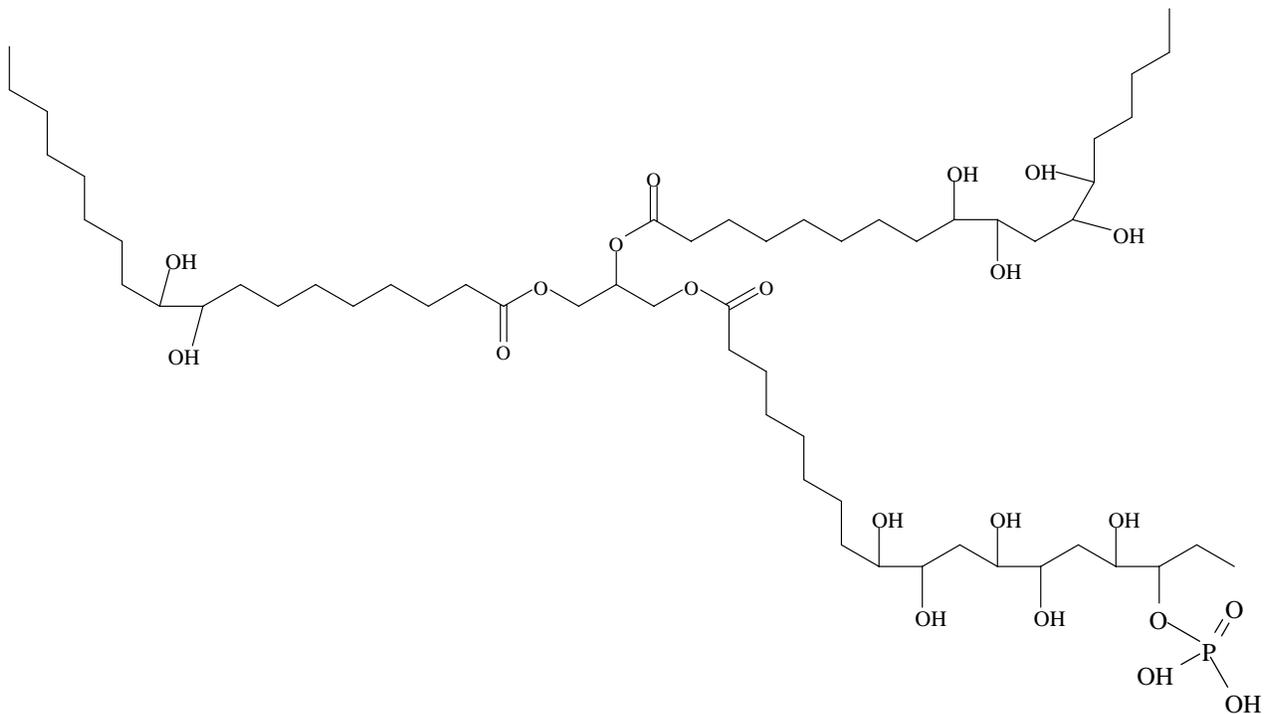


Figure 2. Vegetable Oil Phosphate Ester Polyol (POLYOL)



POLYOL has been shown to be useful as:

- 1) Reactive diluent in epoxy cationic cured reactions (Zero VOC, good properties, low cost)
 - a) radiation cured systems^{17,18}
 - b) bake cured systems¹⁹
- 2) Reactive diluent resin for alkyd and polyesters²⁰ (Reduced VOC, good properties, low cost)
- 3) Hyperbranched polyol for low viscosity, high performance alkyd (Reduced VOC, good properties, low cost)²¹
- 4) Reactive diluent/disperser for waterborne industrial alkyd and polyester coatings⁴ (near zero VOC, good properties, low cost)
- 5) Polyol in moisture cured polyurethane coatings (Low VOC, good properties, low cost)⁵

TxState continued process development, scale-up production of POLYOL, made prototype paints that meet 2006 target VOCs, demonstrated application of the new polyol in paints, and helped commercial partners commercialize POLYOL and the above systems. The expected economics of bulk POLYOL are extremely favorable to the success of the project. POLYOL should cost around \$0.70/lb when made in bulk. Arkema is quoting \$1.50/lb for developmental quantities. Short oil alkyd resins sold in 2002 in bulk for \$0.75 – 2.00 per dry weight pound. A potential saving of 7-40% in resin costs for heat cured paints used in industrial applications. Polyols listed for \$1.00-3.50/lb. A potential savings of 20-70%. Since then, glycerin has fallen to about \$0.50/lb as a by-product of biodiesel production. Coating and paint formulations with zero to 1.8 lb/gal of VOC and good physical properties have been generated.

This new technology should make possible commercial coatings and paints with excellent VOC, good film properties, and favorable economics for the producers and consumers.

Proposed Technology for General Industrial Alkyd Bake Coatings

The coating market share of alkyd paints declined at about 3% per year in the 1990's due to growth of latex paints that have lower VOC. Recently, the higher VOC of alkyd paints has been a major problem. Reduced VOC alkyds generally have reduced performance. Improvement in adhesion and corrosion resistance along with reduced VOC, reduced yellowing, and reduced cost would make high performance industrial alkyd waterborne coatings more viable. POLYOL has the potential to improve adhesion, flexibility, corrosion resistance, and reduce VOC, yellowing, and cost of waterborne and solvent borne alkyd bake coatings for general industrial metal. The proposed technology for waterborne coatings allowed us to reach 2006 VOC targets based on work that gave formulations with 60 g/L VOC and good performance. Use of this technology with exempt solvents should allow similar goals in solvent borne formulations.

¹⁷ R. Raghavachar, G. Sarnecki, J. A. Baghdachi and J. L. Massingill, "Cationic UV Cured Coatings Using Epoxidized Soybean Oil", *RadTech Report*, 12(5), 36-40 1998.

¹⁸ D. Desai, M. Rahim, and J. L. Massingill, Jr., "Cationic UV Cured Coatings Using Epoxidized Soybean Oil", *Proceedings of RadTech2000*, Baltimore, April 2000.

¹⁹ Ramya Raghavachar, Greg Sarnecki, Jamil Baghdachi and John Massingill, "Cationic, Thermally Cured Coatings Using Epoxidized Soybean Oil", *J. Coating Technol.*, **72**(909), 125-133 (2000).

²⁰ Bin Zhong, Maruf Rahim and John Massingill, "Novel Coatings from Soybean Oil Phosphate Ester Polyols", *J. Coating Technol.*, **73**(915), 53-57 (2001).

²¹ J.L. Massingill, unpublished results.

Atmospheric Reactivity of Solvents

Maximum use will be made in this project of solvents, such as t-butyl acetate, that have been shown to have low levels of reactivity in the atmosphere by Dr. William Carter at the University of California Riverside. Where possible, high reactivity solvents will be eliminated. If they can not be eliminated they will be replaced to the extent possible by low reactivity solvents.

Process Development.

POLYOL. We continued to improve the process for making POLYOL and resins from the POLYOL. A solventless process for making POLYOL was demonstrated in the last month of the #8421 research contract. This process was validated, improved, and transferred to Arkema for pilot plant implementation. A new solvent process for POLYOL3.5 was developed to control the viscosity for the high phosphate POLYOL.

Alkyd Resin. A process for making low viscosity, highly branched alkyd resins from POLYOL was demonstrated. A new composition of matter patent could be filed on the hyperbranched alkyd. This alkyd will be water dispersible and useful for meeting 2006 VOC targets.

Pilot Plant Production.

POLYOL. Arkema worked with our laboratory procedure to develop and implement a pilot plant procedure for producing POLYOL in multi-gallon quantities. This consumed about ½ man-year for three years. They have also agreed to commit ½ man-year of technical service personnel to support their product demonstration efforts. Quart, gallon, and 5 gallon quantities of POLYOL are available. Drum quantities of POLYOL were not available when Niemann & Associates requested in 2004 or when Valspar requested in 2005.

POLYOL Sampling Plan. POLYOL sample availability was made known by the following:

- POLYOL was featured at the USB booths at the International Coatings Exposition, the American Oil Chemists Society Annual meeting, and the American Chemical Society Annual meetings each year.
- The hyperbranched POLYOL reactive diluent resin was offered to select customers to confirm its superior combination of performance, low VOC, and economics. Precision Coatings completed the initial screening of POLYOL in container coatings. They were pleased with the results. We worked with Arkema to overcome product variability and to produce pilot plant quantities for the second round of sampling to a broader range of customers.
- POLYOL as a polyurethane polyol was demonstrated in the lab.

PREVIOUS WORK

The Dow Chemical Company taught the process for making epoxidized soybean oil phosphate ester in a 1979 patent that has expired. The PI recognized the potential value of POLYOL in coatings and obtained USB funding to research the process, produce experimental quantities, and demonstrate the value in coatings. The results were much better than anticipated. The phosphate ester portion of the POLYOL did impart improved adhesion to coatings as expected. In addition, the multiple hydroxyl groups provided enough crosslinking to make hard coatings from

historically very soft fatty acid compounds. The POLYOL gives paints that have an outstanding combination of low cost, excellent properties, and low VOC.

Process development. Novel vegetable oil phosphate ester polyols (Figure 2) have been synthesized from partially and fully epoxidized vegetable oils (Figure 1).²² Processes have been developed in order to control oligomer formation and minimize hydrolysis of the glyceryl ester bonds. The resulting phosphate ester polyols had several types of functional groups-- polyols for hydroxyl-cure mechanisms, unsaturation for oxidative crosslinking, and the phosphate ester group for adhesion and water-reducibility. Our new processes cover a range of phosphate epoxy ratios and produce phosphate ester polyol with very little free fatty acid and no solvent.

Alkyd Bake Coatings. The results of formulation work showed that these polyols can be successfully incorporated into both solvent borne 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. This research project, along with 2 others, was initially funded from May 1998- June 2000 with a research grant for \$343,000 from the United Soybean Board. A USB extension contract for one year has been granted that will cover POLYOL and three uses. This proposed project will complement USB funding and focus effort on waterborne and solvent borne alkyds that meet 2006 VOC targets.

Experimental

Materials. Three experimental types of epoxidized soybean oil (ESBO)-1/3 ESBO, 1/2 ESBO, and 2/3 ESBO- and commercial, fully epoxidized ESBO or 3/3 ESBO (Vikoflex 7170, EEW 231) were kindly supplied by Elf Atochem (Table 1). Cellokyd™ 2849-X (a high solids short oil TOFA alkyd) was supplied by REICHOLD. 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 ethanolamine (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 water-borne alkyd resin based on core shell technology, it is 38% in water containing 5.6% 2-butoxy ethanol (EB). [Note: A new version of Resydrol 586 W with no solvent may make a zero VOC waterborne high performance alkyd possible]. 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.

Solvent borne Coatings. A commercial alkyd and starter coating formulation (Table 2) were employed to test the effect of POLYOL on coating properties. Based on this original recipe, the

²² G. Sarnecki, et al., "Coatings from Soybean Oil Polyol I. Preparation", Amer. Oil Chem. Society National Meeting, 1998.

alkyd resin was replaced with POLYOL 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 POLYOL, 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. After 5 minutes mixing, distilled water was added slowly into the mixture. Stirring was continued for 30 minutes after all the water had been added. The color of the coatings changed from milky white to milky yellowish. The resulting emulsion had a pH range of 8-9 and was about 55 % NVW. The pH was adjusted by addition of DMEA as needed.

Panel Preparation. Q-Steel panels (R-36) were wiped with MEK (methyl ethyl ketone), and allowed to dry. The coatings were applied with a bird blade draw down bar. Solvent borne coatings were 2.0 mil wet film thickness and water-borne coatings were 0.6 mil wet film thickness. The coated panels were left at room temperature for 5-10 minutes before putting in the oven to bake for 30 minutes. Solvent borne 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. VOC of formulations was determined by U.S. EPA test method. Acid number (A.N., ASTM D1639), hydroxyl number (OH#, ASTM D1957), Epoxy value (E.V., ASTM D1652), Pencil hardness (ASTM D3363-92a), Crosshatch adhesion (ASTM D4752), Solvent resistance (ASTM D 5402), impact resistance (ASTM D2794-92) and Non-volatile weight (NVW, ASTM D2369) 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 seconds for two times.

Results

Solvent borne Coating Systems. A commercial solvent borne 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. Fs₁ was the formula recommended by the resin supplier. For formulas Fs₂-Fs₅, the ratio of Alkyd/POLYOL was 50/50 and the ratio of (Alkyd+POLYOL)/Cymel was 50/50. Fs₁ was cured at 175°C for 30 minutes while the bake temperature of the POLYOL formulations was reduced to 145°C for 30 minutes. Film appearance of all the coatings was smooth and glossy with no surface defects.

The results show that POLYOL 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 POLYOL as the only resin in the coating, we obtained a coating with medium properties, shown as Fs₆. We conclude from Table 2 that:

- 1) POLYOL is a good, environmentally compliant co-resin, which can reduce the VOC of coatings.

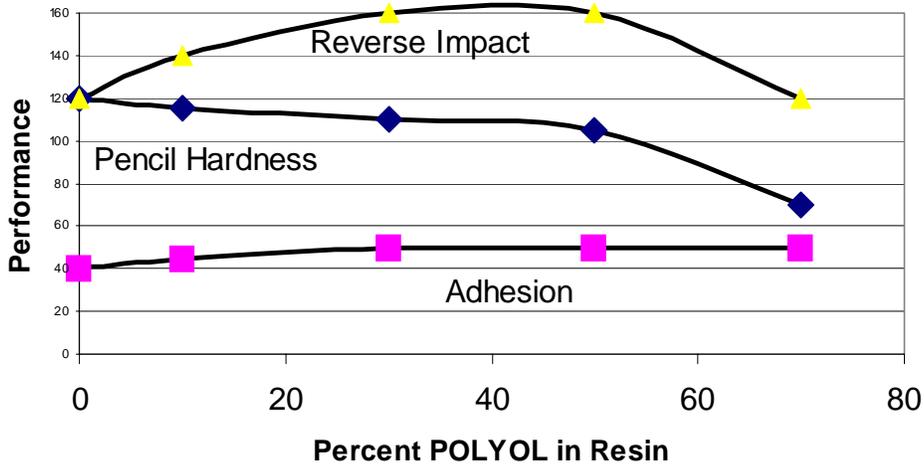
- 2) Adhesion was improved for POLYOL formulations.
- 3) POLYOL coatings had solvent resistance equal to the standard.
- 4) The POLYOL formulation gave a coating with increased impact resistance.
- 5) Polyol made from fully epoxidized soybean oil gave a pencil hardness slightly less than the standard.
- 6) POLYOL gave excellent over bake resistance.
- 7) A coating made of only POLYOL and crosslinker can give coatings with medium properties.
- 8) Using exempt solvents could potentially produce solvent borne formulations that meet 2006 VOC targets.

Table 2. Formulations of POLYOL in Alkyd Coatings

	FS ₁	FS ₅	FS ₆
Degree of Epoxidation	-	3/3	3/3
Cellokyd 2849-X	24	12	-
POLYOL	-	12	24
Cymel 303	24	24	24
Cymel 4040	0.02	0.02	0.02
BYK361	0.02	0.02	0.02
Xylene	5.0	5.0	5.0
MEK	2.0	2.0	2.0
PROPERTIES			
Viscosity (cPs)	380	392	406
NVW (%)	77	79	78
VOC (lb/gal)	2.03	1.87	1.84
Film thickness(mil)	1.0	1.1	1.0
Pencil hardness	4H	2~3H	B
MEK double rubs	>200	>200	35
Adhesion	4B	5B	3B
Impact resistance (D/R)	140/120	160/160	120/100

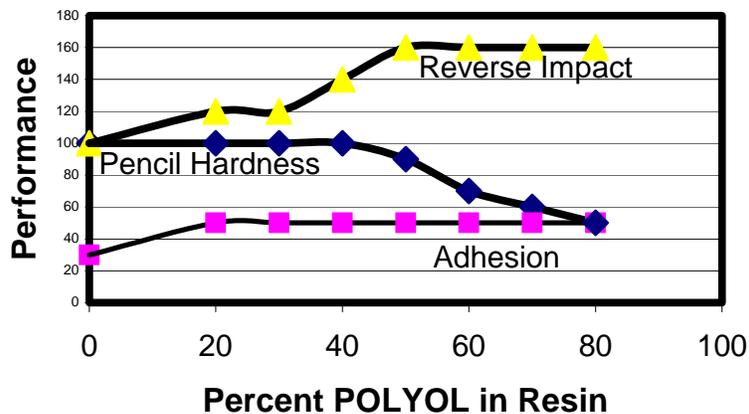
We investigated POLYOL in formulations with different Alkyd/POLYOL ratios using from 10-70% POLYOL as the resin. The results in Figure 3 show that 10-50% POLYOL in the alkyd coating was acceptable and could give lower VOC, better adhesion, and better impact resistance at some sacrifice of hardness. Even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

Figure 3. Effect of Alkyd/POLYOL Ratio



Waterborne Coating Systems. A commercial waterborne alkyd resin was employed to investigate the properties of POLYOL in water-reducible coatings. The results in Figure 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% POLYOL. Solvent resistance was equal even at an Alkyd:POLYOL ratio of 20:80. Up to 40% POLYOL can be incorporated without sacrifice of hardness while the impact resistance was improved with increasing amount of POLYOL in the formulation. Resydrol AY 586W is a high performance waterborne alkyd based on a core-shell technology that retailed for approximately \$2.00/lb in 2002. It contains less than 6% solvent. The formulation with 50% POLYOL replacing the Resydrol **contains less than 3% solvent** and its cost is reduced by about 50%. This formulation meets 2006 VOC targets.

**Figure 4. Effect of POLYOL:Resin Ratio
 Waterborne Coating**



A standard coating based on commercial water-borne 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.

Table 6. Effect of 40% POLYOL in Commercial Resin

Alkyd:POLYOL Ratio	100:0	60:40
Coating properties		
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 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 3 weeks at 50 °C.

Conclusions- Alkyd Coatings

Vegetable oil phosphate ester polyols were synthesized successfully and incorporated in bake coatings with excellent results. The resinous hyperbranched POLYOL is 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

POLYOL can be incorporated into solvent borne coatings with lower VOC, good adhesion, and improved impact resistance. Use of proposed exempt solvent t-butyl acetate in these formulations would meet 2006 VOC targets.

For water-reducible coatings, POLYOL 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. Waterborne formulations in the proof of concept formulations had VOC that meet 2006 VOC targets and had good hardness.

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

Work during this Project

During this project phosphate ester content of coatings was optimized for maximum corrosion resistance and a one pack ambient moisture cured polyurethane coating was formulated using POLYOL. The work is summarized in the following two papers.

I. Self-Emulsifiable Soybean Oil Phosphate Ester Polyols for Coating Applications

Yinzhong Guo²³, Vijay M. Mannari²⁴, Pulin Patel, and John I. Massingill Jr.²⁵
*Institute for Environmental and Industrial Science, Texas State University,
San Marcos, Texas 78666*

ABSTRACT:

A series of soybean oil phosphate ester polyols (SOPEP) were prepared by reaction of fully epoxidized soybean oil with phosphoric acid and simultaneous hydrolysis, in presence of a polar solvent. The polyols were characterized by determination of acid value, oxirane number, hydroxyl value, molecular weight (GPC), and FTIR spectra. These polyols with varying amount of acid phosphate groups could be self-emulsified to form aqueous dispersions after neutralization with organic base. These aqueous dispersions showed varying degrees of stability and their appearance ranged from opaque dispersions to translucent to clear solutions. Waterborne coating compositions have been prepared using these aqueous dispersions as principal components and their thermally cured film properties have been studied. It has been found that by careful selection and formulation, SOPEP can be successfully used for low VOC waterborne coating formulations. SOPEP with 3.5% phosphate ester content shows remarkably superior corrosion resistance properties.

Soybean oil is the most readily available and one of the lowest cost vegetable oils in the world. There is currently significant interest in the use of soybean oil as a component in printing inks¹ as plasticizers^{2,3} and stabilizers in the manufacture of plastic parts due to its environmentally friendly, biodegradable, and non-corrosive properties. Moreover, it is increasingly attractive to incorporate soybean oil for making water dispersible polymers and resins for packaging films and curing agents used in surface coatings⁴ which are more energy conserving and environmentally desirable than solvent based paints.⁵ Epoxidized soybean oil (ESBO), which is an oxidation product of soybean oil with hydrogen peroxide and either acetic or formic acid, has been investigated as an epoxy resin in UV cured coatings.^{6,7} Recently, ESBO has been an attractive option for use in high solids, low/zero VOC thermal cure coatings owing to its low viscosity, commercial availability, low cost, and numerous reactive oxirane groups.

Our group has investigated direct incorporation of ESBO into UV-cure systems as an additional epoxy component.⁸ We also succeeded in preparing soybean oil phosphate ester polyols (SOPEP) by careful hydrolysis of ESBO with phosphoric acid as catalyst and incorporating them into low VOC industrial bake coatings possessing improved adhesion properties due to the presence of the phosphate ester groups.^{9,10} Furthermore, the authors have investigated the effects of catalysts, solvents, amount of water on the hydrolysis of ESBO.¹¹ Cationic UV-cured coatings of epoxide-containing soybean oils have been found that can provide

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corrosion resistance.¹² The polymeric structure has great effect on the adhesion and corrosion resistance of epoxy coatings.¹³ It has been also known that solvent-borne advanced epoxy phosphate esters of bisphenol diglycidyl ethers containing 1% phosphoric acid give coatings with improved adhesion, flexibility, and corrosion resistance¹⁴. In the present work, the self-emulsification of the neutralized soybean oil phosphate ester polyols and their application for water based coatings were further investigated.

EXPERIMENTAL

Materials.

Epoxidized soybean oil (Vikoflex™ 7112 Ex Atofina- Iodine value -1.35, Acid value 0.08mg KOH and % oxirane oxygen- 7.0) was used as supplied. Commercial alkyd resin, Beckosol™ 12-054 and aminoplast cross-linker (Resimene™ 747) were supplied by Reichhold, Inc. Catalyst, Cycat™ 4040, was obtained from Cytec. The test panels used were B-1000 from Q-panel, Inc. All other chemicals were supplied by Aldrich Chemical Co. and were used without further purification.

Synthesis of Soybean oil phosphate ester polyols.

Soybean Oil Phosphate ester Polyols (SOPEP) were prepared by reaction of ESBO with Phosphoric acid and water, in presence of a polar organic solvent. The process involved addition of phosphoric acid, at controlled rate, to the mixture containing ESBO, solvent and water, under mechanical stirring. A series of SOPEP was synthesized using amount of phosphoric acid varying from 2.0 to 30 % by wt of ESBO. The reaction temperature for synthesis of SOPEP varied from of 25-85 °C. The reaction was monitored by periodic determination of percent oxirane oxygen content and acid value of the sample. Upon completion of the reaction, solvent and residual water were removed using rotary vacuum evaporator. Un-reacted phosphoric acid was removed by successive washing the ethereal solution of the product with water. SOPEPs were then characterized for various physical, chemical and spectroscopic parameters. (Table 1).

Preparation of Aqueous dispersions of SOPEP:

SOPEP was neutralized with calculated amount of amine (based on 100% neutralization) under stirring at room temperature. Dimethylethanolamine was used as amine neutralizer. Deionized water was added slowly to the neutralized SOPEO under high-speed disperser, at 2000 rpm. The mixture was stirred for 30 minutes after addition of water was complete. The resultant dispersions were milky to translucent to clear solution depending upon phosphate ester content of the product. All the dispersions were prepared to have 50% SOPEP, with no co-solvent. It was found that the samples between 3.0 to 4% phosphate ester content formed stable emulsions in water, those between 4 -10 % were translucent, while those with >10% dissolved in water and gave clear solutions.

Characterization of Polyols: Acid values (A.V.), oxirane numbers (O.N.), hydroxyl values (H.V.) of the SOPEP samples were determined by ASTM methods (ASTMD 1639-90, ASTMD 1652-97, and ASTMD 1957-86, respectively). The viscosities of the samples were measured using Brookfield viscometer at 25°C. The molecular weight was determined by Gel Permeation chromatography (GPC) using a polystyrene standard. The SOPEP samples were also characterized with FTIR spectra. Corrosion resistance test was carried out as per ASTM-B-117, for 96 hrs.

RESULTS AND DISCUSSION

SOPEPs with different phosphate ester content:

In this paper the term phosphate ester content is used to indicate the amount of phosphoric acid used in the synthesis of SOPEP. A series of Soybean oil phosphate ester polyols with varying phosphate ester content (2, 3, 4, 5, 6, 8, 10, 20, 30 weight %) have been synthesized from fully epoxidized soybean oil using phosphoric acid and water, in presence of a polar water miscible solvent. The characteristics of product SOPEP are summarized in Table1. For all the samples synthesized, Oxirane Number (% by wt of oxirane oxygen) has been used to monitor the progress of reaction and all the reactions were continued till Oxirane Number was less than 0.1%.

As expected, increasing the amount of phosphoric acid increased acid value of the products. This indicates the formation of acid phosphate, both mono and di-phosphate esters. We believe that under the conditions of reaction, equilibrium reaction involving formation of mono, di and tri phosphate esters and their hydrolysis is taking place.

In Table-1, the values of molecular weight and polydispersity index for all the products clearly indicate the formation of polymeric or oligomeric species. Increase in molecular weight is thought to be resulting from the intermolecular phosphate ester formation. However, the significantly lower hydroxyl values, as compared to the theoretical values, indicate oligomerization through epoxy-epoxy reaction. Epoxy compounds are known to undergo such reactions through acid catalyzed cationic mechanism.^{7, 9} There is no specific trend observed for the hydroxyl value as a function of amount of phosphoric acid added, and resultant products have almost constant hydroxyl values. This might be due to increased rate of oligomerization at higher acid contents, resulting into lower hydroxyl values.

Table 1. Percent Phosphate Ester vs. Properties of SOPEP

%PO ₄ →	2	3	4	5	6	8	10	20	30
O.N. (%)	0.07	0.06	0.04	0.03	0.04	0.03	0.02	0.02	0.01
Acid No. (mg KOH)	11.8	26.4	32	59.7	65.9	89.2	104	132	176
Hydroxyl # (mg KOH)	258	253	244	260	255	263	259	256	279
Viscosity cPs@50C	5250	8700	1687 *	4790	4410	3160	4350	2690	2310
Mw	3770	6813	7125	7917	7285	3918	2717	-	-
Mw/Mn	1.8	2.7	2.8	2.7	2.8	2	1.7	-	-

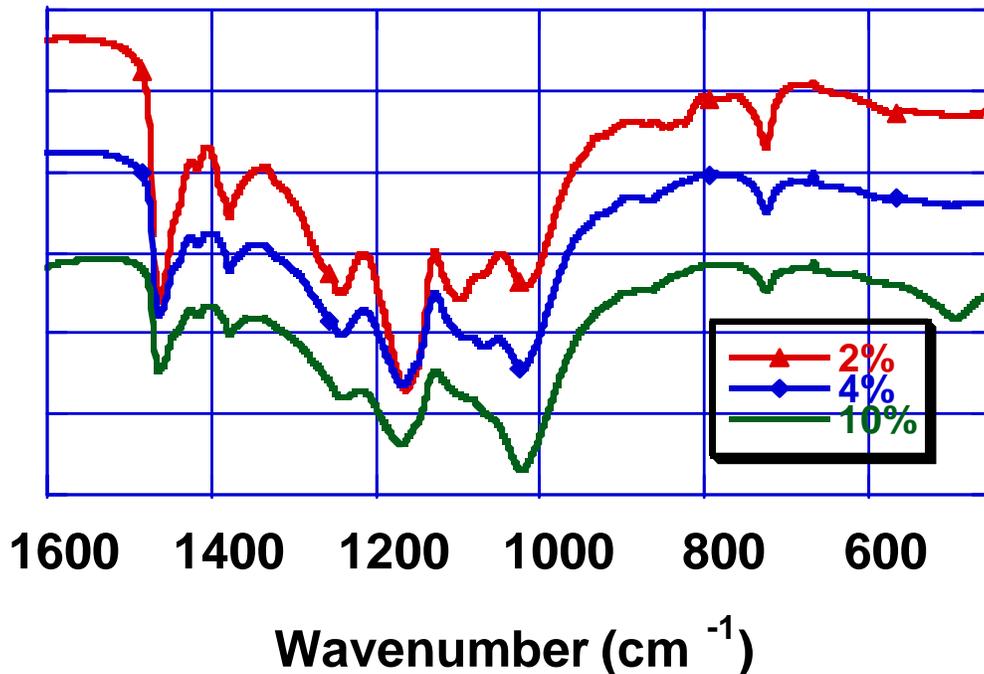
* 14% solvent

It is interesting to note the products containing above 6% phosphate ester exhibit lower viscosities and molecular weights. We attribute these characteristics to an enhanced rate of di-/tri-ester hydrolysis in this exceedingly acidic medium. Further, increased phosphate ester content will reduce the epoxide group concentration on the oil molecule, resulting into reduced rate of molecular weight building oligomerization reaction.

The FTIR spectra of these polyols (Fig.1) gave the disappearance of the peak at 824cm⁻¹, indicating the loss of the epoxy groups, and two characteristic peaks appeared at 3400cm⁻¹ (-OH groups) and 1020cm⁻¹ (phosphate groups). Figure 1 shows the peak change at 1020cm⁻¹ of the SOPEP with phosphate ester content of 2%, 4%, and 10%. The most noticeable feature of the

spectra is the increasing intensity of the peak at 1020 cm^{-1} as a function of phosphate ester content, indicating the presence of increasing degrees of phosphate incorporation.

Figure 1. FTIR Spectra for SOPEP



Aqueous Dispersions of SOPEP

SOPEPs containing ionizable acid phosphate groups are thought to be capable of self-emulsification in water, after neutralization with suitable amines. N,N-dimethylethanolamine (DMEA), which is widely used as neutralizer for carboxylic acid containing polymers, has been used for the present study. The aqueous dispersions made from different samples showed different behavior. SOPEPs having less than 3% phosphate ester content showed poor emulsion stability and resulted into phase separation within 24hrs of their preparation, while those with 3% and 4% yielded opaque and stable dispersions. Samples between 4% and 10% were stable translucent and those above 10% phosphate ester content were clear solutions. These results are not surprising since with increasing phosphate ester content, the acid values of the samples are increasing and hence upon neutralization with base, they become increasingly hydrophilic.

Formulation of coatings and film properties:

Water-borne coating formulations were prepared using the aqueous dispersions of SOPEPs as principal binder component. Hexamethoxymethyl melamine (HMMM) was used as cross-linker. Aromatic sulfonic acid was used as curing catalyst. All the coatings were formulated have SOPEP/HMMM weight ratio of 70/30. The baked film properties of these compositions are shown in Table-2. The films of the compositions containing SOPEP with > 8% phosphate ester content showed significant wrinkling and poor adhesion and hence other properties could not be tested and reported.

The results in Table-2 indicate that while all the films have good hardness, they lack in adhesion and impact resistance properties. This indicates that films are too brittle, probably due to very high cross-link density. It is also possible that under the conditions of curing, HMMM might have undergone excessive self cross-linking. We attributed these results mainly to higher HMMM content in the compositions. To study the effect of reduced HMMM amount, another series of compositions were prepared with SOPEP/HMMM weight ratio of 80/20. A typical formulation is shown in Table-3.

Table 2. Film Properties of SOPEP based Water-borne Compositions*

SOPEP	SOPEP3	SOPEP3.5	SOPEP4	SOPEP6	SOPEP8
Dry-film thickness (mil)	0.8	0.9	0.7	0.7	0.8
Pencil Hardness	6H	6H	6H	6H	6H
Impact resistance (D/R) (inch*lb)	80/30	90/30	60/20	60/20	60/20
MEK double-rub	> 200	> 200	> 200	> 200	> 200
Adhesion (cross-hatch)	1B	1B	1B	1B	1B

* Cured at 140 Deg. C for 30 min.

**Table 3.
 Typical Coating Composition.
 (SOPEP/HMMM ratio -80/20)**

Ingredients	Parts by wt.
SOPEP Dispersion (50% NVM)	72.00
Resimene 747*	9.20
Cycat-4040**	0.60
Surface wetting Additive	0.20
water	18.00
Total	100.00

* Ex-Solutia, ** Ex-Cytech Industries

The results of the film properties of two selected compositions are presented in Table-4. These results indicate that it is possible to formulate coating compositions by varying SOPEP/HMMM ratio to yield useful film properties. However, it appears that there exists an optimum level for phosphate ester content above which film properties become inferior.

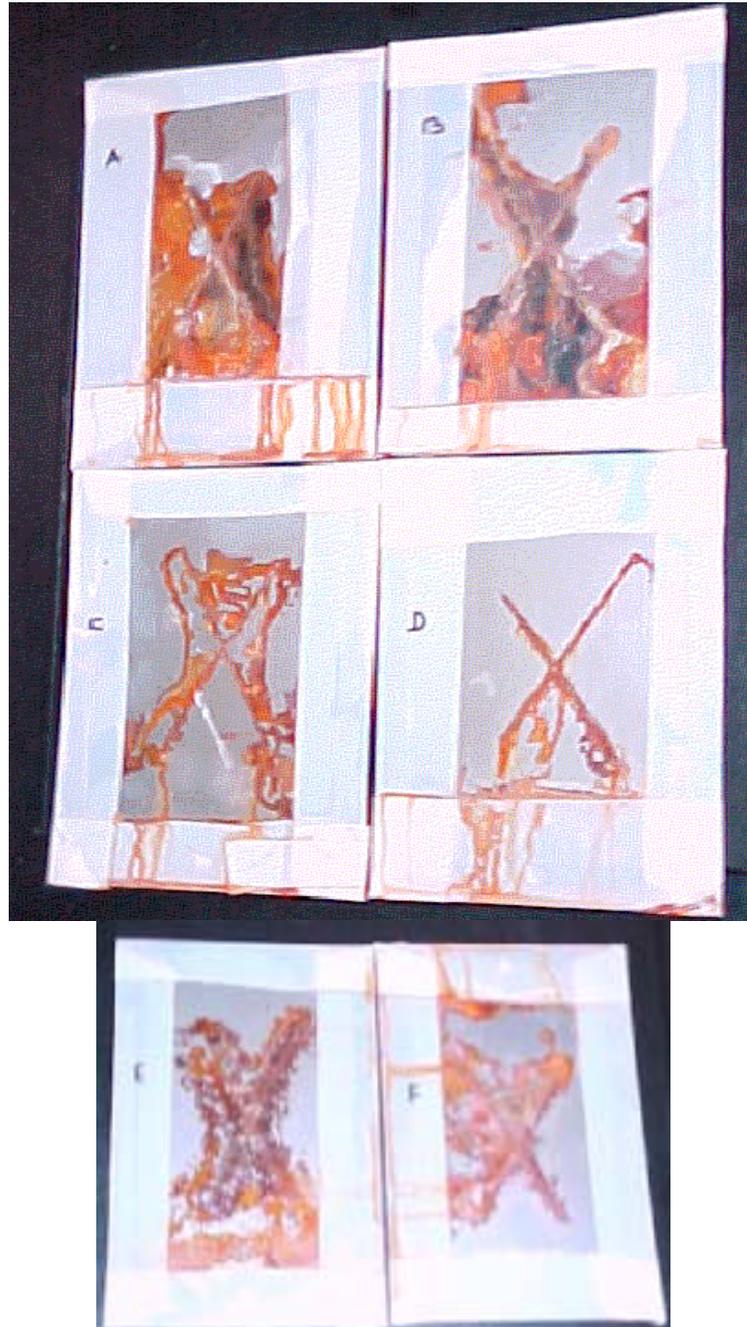
**Table 4. Film Properties of SOPEP based Water-borne Compositions
 (SOPEP/HMMM = 80 / 20)**

SOPEP	SOPEP3.5	SOPEP5
Dry-film thickness (mil)	0.9	0.9
Pencil Hardness	3H	3H
Impact resistance (D/R)	160/90	100/60
MEK double-rub	150	100
Adhesion (cross-hatch)	4B	2B
* Cured at 140 Deg. C for 30 min.		

Corrosion resistance: Since phosphate esters are known to improve corrosion resistance properties of the coatings on metallic substrates ¹⁵, it was thought to be interesting to study the effect of phosphate ester content on corrosion resistance properties. The SOPEPs having 3, 3.5, 5, and 8% phosphate ester content were selected for these study. The coating compositions (SOPEP/HMMM weight ratio of 80/20) were applied on untreated cleaned steel panels and cured at 140 deg C for 30 min. The panels were evaluated for salt fog corrosion resistance, as per ASTM -117-B test method for 96 hrs. Two commercial water-borne alkyd coatings were also evaluated under identical conditions, for comparison. Fig.-2 shows the photographs of coating films on the panels after salt fog corrosion test (96 hrs).

The results show that composition containing 3.5% phosphate ester content (photograph D), has superior corrosion resistance among all the samples studied. Further, this is also better than commercial alkyd coatings. Theoretically, the more phosphate gives the better adhesion and corrosion resistance of the coating film. The poor corrosion resistance of high phosphate containing compositions might be due to higher hydrophilicity of the polymer. It is believed that phosphates ester groups that could not orient to substrate-coating interface (due to the possible saturation at the interface), would increase water sensitivity of the coating.

Figure 2. Corrosion Resistance Test (ASTM -117-B, 96 hrs)



- A. Commercial Waterborne Alkyd
- B. Commercial Solvent borne Alkyd
- C. SOPEP 3% PO₄
- D. SOPEP 3.5% PO₄
- E. SOPEP 5% PO₄
- F. SOPEP 8% PO₄

CONCLUSIONS

It is possible to synthesize polymeric / oligomeric polyols, varying in phosphate ester content, from epoxidized soybean oil. It is possible to derive self-emulsifying polyols from these SOPEPs by neutralization of the acid phosphate groups with suitable amines. By selection of proper acid value of SOPEP, it is possible to produce stable aqueous dispersions of SOPEP having wide range of properties. These stable aqueous dispersions can be used as principle component of thermally cured coating compositions with melamine type cross-linkers. By proper selection of type and amount of SOPEP and cross-linker, it is possible to formulate water-borne coatings with useful film properties. Besides low cost and low VOC of such coatings, SOPEP containing 3.5% phosphate ester content exhibited substantially improved corrosion resistance properties.

ACKNOWLEDGMENT

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II. TWO-COMPONENT HIGH-SOLID POLYURETHANE COATING SYSTEMS BASED ON SOY POLYOLS †

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ABSTRACT

Soybean Oil based polyols – Soybean Oil Phosphate Ester Polyols (SOPEPs), having varying hydroxyl content and viscosity have been prepared as low cost and low VOC polyols for coatings applications. These SOPEPs have been used as hydroxyl component of “two-component Polyurethane (2K-PU)” coating compositions and their film properties were studied. Blends of commercial polyester polyol and SOPEP in varying proportions were also used to formulate PU coatings. Their film properties were studied and compared. We found that SOPEP can be used as the sole hydroxyl component or as reactive diluent for polyester polyols in 2K-PU coating systems. SOPEP is derived from a relatively inexpensive and renewable resource and use of SOPEP can substantially reduce VOC and cost of PU coating formulations.

Introduction

Polyurethanes (PU) have found extensive applications in the coating industry mainly because they exhibit excellent abrasion resistance, toughness, low temperature flexibility, chemical and corrosion resistance, and a wide range of mechanical strength. Because of these characteristics PU coatings have emerged as coatings of choice for applications from industrial maintenance to automobile finishing to chemical resistant coatings.¹⁻² Two-component Polyurethane (2K-PU) systems are especially attractive since they offer flexibility in formulation which enables customizing demanding end-use requirements.

Polyols are major components of PU coating systems and are often designed to suit the performance requirements of the intended applications. Among the common commercially available polyols for 2K PU systems are hydroxyl-functional polyesters, hydroxyl functional acrylics, and polyether polyols. Polyesters and acrylics produce very tough polyurethane films under proper curing conditions and are among the most widely used polyols for high performance coatings. Polyether polyols are generally used in highly flexible systems such as sealants and other non-coating applications.

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In recent years, there has been renewed interest in developing materials and products based on bio-based and renewable resources. The principal drivers for this, among others, include environmental, regulatory and economic factors. A recent study indicates that soy based polyols have about 25% of the total environmental impact of the petroleum based polyols and that use of soy polyols will result in significant reductions in global warming, smog formation, ecological toxicity, and fossil fuel depletion.³ Preparation of polyols from vegetable oils has been extensively reported in the literature.⁴⁻¹³ A variety of chemical modifications to vegetable oils have been studied to derive multiple hydroxyl functional derivatives. Guo *et. al.*¹⁴ reported preparation of soy-polyols by the hydrogenation of hydroformylated soybean oil and studied the physical and mechanical properties of polyurethanes based on these soy-polyols.

Petrovic *et. al.*¹⁵ have prepared a series of polyurethanes from halogenated, hydrogenated, and methoxylated epoxidized soybean oil with average OH functionality of 3.7. Polyurethanes based on non-halogenated soy polyols showed higher thermal stability but lower glass transition and mechanical properties. Guo *et. al.*¹⁶ report that PU foams based on polypropylene oxide polyols and those based on soy polyols have comparable mechanical and thermoinsulating properties, that the soy polyol foams were more stable toward both thermal degradation and thermal oxidation. The lack of ether linkages in the soy-based polyols is thought to be the origin of improved thermal and thermo-oxidative stabilities of soy-based PU foam. Petrovic and Javni¹⁷ report the use of soy polyols with PU prepolymers made from epoxidized soybean oil and polymeric 4,4'-diphenylmethane diisocyanate to make coatings with good adhesion and hardness. Gerbase *at al.*¹⁸⁻¹⁹ have studied and reported different methods to functionalize vegetable oils in order to derive bio-renewable materials.

Our research group has primarily focused on epoxidized vegetable oils for deriving soy-polyols using phosphoric acid as modifying agent. Synthesis of soybean oil phosphate ester polyol from epoxidized and partially epoxidized soybean oil have been previously reported.²⁰⁻²¹ The processes have been developed to control oligomer formation and minimize hydrolysis of the glyceryl ester bonds in ESBO. SOPEP from ESBO with various epoxy values have been made and formulated in coatings. The film properties of the baking compositions based on these polyols were studied for both solvent borne and water borne systems.²² Low cost systems with good physical properties and excellent adhesion were reported.

In the present study, we have derived soy-polyols containing phosphate ester groups with varying OH contents, from epoxidized soybean using phosphoric acid as catalyst and modifying agent. In the present work, a series of SOPEPs with hydroxyl contents varying from 3.6% to 7.3% have been synthesized from epoxidized soybean oil. The film properties of 2K-PU coatings systems containing these polyols are studied.

Materials:

Partially epoxidized soybean oil (3.5% oxirane oxygen) and fully epoxidized soybean oil (7.0% oxirane oxygen) were supplied by ATOFINA. Aromatic isocyanate prepolymer DESMODURTM E 744 (diphenylene-4,4'-diisocyanate (MDI)-based) and aliphatic polyisocyanate DESMODRTM Z 4470 BA (isophorone disocyanate (IPDI)-based) were provided by Bayer Corporation. The properties of isocyanate compounds are shown in Table-1. Polyester polyol DESMOPHENTM 651A-65 was procured from Bayer (%OH content-5.2, NVM by wt.-65%, Acid number-3.0). Tertiary Butyl Acetate, TBACTM, was provided by Lyondell Chemical Company. Dibutyltin dilaurate, xylene, super phosphoric acid, isopropyl alcohol and methyl ethyl ketone (MEK) used in

the study are analytical grade chemicals (Aldrich) and used as received. The test panels (6" x 4" x 0.032") used for the study of film properties were standard low carbon, cold rolled steel (dull matte finish), complying with ASTM A366, supplied by Q-panel Company.

Table-1: Properties of the Isocyanate components use for the Coatings

Properties	DESMODUR Z4470 BA	DESMODUR E744
Chemistry	IPDI-based Aliphatic Polyisocyanate	MDI-based Aromatic Polyisocyanate
Appearance	Clear, slightly yellow liquid	Clear brownish yellow liquid
NCO content, %	11.9	23.2
Viscosity @ 25deg.C, mPaS	600	360
Solids, %	70.0	100.0
Equivalent weight (as supplied)	353	179
Specific gravity @ 25 deg C, g/cm ³	1.05	1.21

Synthesis of Soybean Oil Phosphate Ester Polyols (SOPEPs)

All the reactions were carried out in either a 250ml or 500 ml 4-necked flask equipped with a variable speed stirrer, a thermometer, an inert gas inlet tube, a condenser, and a dropping funnel. Flasks were heated with electric heating mantles connected to a variable voltage transformer. A general method for synthesis of SOPEP is described below.

ESBO (150.0g) and 2-propyl alcohol (75% to 90% based on weight of ESBO) were charged into a 500 ml reaction flask under agitation. Super phosphoric acid (from 2% to 4% based on weight of ESBO) dissolved in distilled water (15.0 g) was added to the flask from a dropping funnel at controlled rates of addition (30-45 min). Temperature during addition of phosphoric acid solution varied from 50°C -100°C for different samples. After addition was complete, reaction mixture was stirred at 70°C -80 °C until the residual oxirane content reached the desired endpoint. Progress of the reaction was monitored by testing a sample for percent oxirane content at regular intervals, by chemical method.²³ Heating was stopped when percent oxirane oxygen content reached less than 0.2%. The un-reacted water and solvent were then distilled off under a rotary vacuum evaporator. The characteristics of the SOPEPs thus prepared are presented in Table-2. SOPEP-I, III, and IV were synthesized from fully epoxidized Soybean oil (7.0 % oxirane oxygen) using 1%, 2% and 4% Phosphoric acid. SOPEP-II was prepared from partially epoxidized (3.5% oxirane oxygen) using 2% phosphoric acid.

Table 2. Properties of SOPEP Samples

Characteristics	SOPEP-I	SOPEP-II	SOPEP-III	SOPEP-IV
Viscosity @ 70 deg (Poise)	22.70	9.00	27.00	12.90
Specific Gravity	1.010	0.997	1.006	1.001
% Volatile matter (by wt.)	0.05	0.10	0.20	0.20
Hydroxyl Content %	4.36	4.70	5.45	7.64
Hydroxyl Equivalent Weight g.	389.9	361.7	311.9	222.5
Acid Value (mgs of KOH)	1.75	14.70	12.00	9.20

Characterization of SOPEP

SOPEP samples were characterized for Acid Value (ASTM-D1639), Hydroxyl value (ASTM-D1957), % oxirane oxygen content (ASTM 1652-73, Method-1), viscosity (ICI Cone & Plate viscometer), and percent volatile content. Table-2 shows the characteristics of the different samples of SOPEP prepared and used in this study.

Coating Compositions

2K PU coating compositions formulated and studied from different SOPEPs are shown in Table 3. Compositions Ar-I to Ar-IV are based on aromatic polyisocyanate whereas Al-I to Al-IV are based on aliphatic polyisocyanate.

Table 3 PU Coating Compositions Based on SOPEP

Components	Compositions , % by weight							
	Ar-1	Ar-II	Ar-III	Ar-IV	Al-1	Al-2	Al-3	Al-4
SOPEP-I	49.70				39.70			
SOPEP-II		48.55				41.40		
SOPEP-III			45.80				35.45	
SOPEP-IV				39.90				32.30
Aromatic Polyisocyanate	25.11	26.30	29.00	34.92				
Aliphatic Polyisocyanate					40.15	44.86	45.05	56.70
Tert Butyl Acetate	25.04	25.00	25.05	25.03	19.95	13.54	19.30	10.80
DBTL	0.15	0.15	0.15	0.15	0.20	0.20	0.20	0.20
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
% NVM	74.96	75.00	74.95	74.97	68.01	73.00	67.19	72.19
Specific Gravity	1.01	1.01	1.01	1.02	1.00	1.00	1.00	1.02
Volume Solids	70.84	71.01	70.70	70.48	63.99	69.60	63.07	68.49
VOC (%by wt)	25.04	25.00	25.05	25.03	32.00	27.00	32.82	27.81
VOC (g/L)	0.00	0.00	0.00	0.00	119.98	135.04	134.88	172.84

We used IPDI based aliphatic polyisocyanate since an initial study indicated very slow reactivity of hydroxyl groups of SOPEP with polyisocyanates based on hexamethylenediisocyanate (HDI). IPDI based polyisocyanates are known give harder films and faster drying as compared to HDI based polyisocyanates.²⁴ These polyisocyanates are, therefore, generally recommended for their use with alkyd type of resins (flexible co-reactants). Due to structural similarities of alkyds with SOPEP, IPDI based polyisocyanate was chosen. 2K-PU coating compositions were also prepared by using a blend of commercial polyester polyol and SOPEP-IV in varying proportion, to study the effect on film properties. These compositions are shown in Table-4. SOPEP-IV was selected for this study because its hydroxyl content was comparable to that of the commercial polyol. The polyester/SOPEP-IV blend was employed as hydroxyl component with both aromatic (PS-25-Ar to PS-100-Ar) and aliphatic polyisocyanate (PS-25-AI to PS-100-AI). All the coatings were formulated having isocyanate index of 1.10.

All the compositions were formulated to have viscosities between 2.0 to 3.0 poise at 25°C, to enable comparison of their non-volatile content and VOC at application viscosity. Dibutyltin dilaurate was used as catalyst for the curing reaction.

Table 4 PU Coating Compositions Based on Polyester/SOPEP Blends

Components	Compositions , % by weight							
	PS-25-Ar	PS-50-Ar	PS-75-Ar	PS-100-Ar	PS-25-AI	PS-50-AI	PS-75-AI	PS-100-AI
Polyester polyol (70%)	13.85	25.55	34.80	40.15	10.30	19.05	26.00	30.18
SOPEP-IV	26.95	16.60	7.60		20.00	12.45	5.72	
Aromatic Polyisocyanate	31.90	29.75	27.30	24.00				
Aliphatic Polyisocyanate					47.50	44.50	41.50	36.15
Tert Butyl Acetate	27.20	28.00	30.22	35.77	22.08	23.88	23.68	23.58
Xylene							3.00	10.00
DBTL	0.10	0.10	0.08	0.08	0.12	0.12	0.10	0.09
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
% NVM	67.95	63.06	57.60	50.18	60.07	56.10	51.77	45.01
Specific Gravity	1.03	1.03	1.03	1.02	1.00	1.01	1.01	1.00
Volume Solids	62.39	56.62	50.30	42.14	54.96	50.35	45.42	38.19
VOC (%by wt)	32.05	36.94	42.40	49.82	39.94	43.90	48.23	54.99
VOC (g/L w/o TBAC)	49.75	92.31	125.84	143.80	178.98	201.36	247.06	313.07

Application and Testing of Film properties

The hydroxyl component and isocyanate components were thoroughly mixed just before the application of their films on the steel panels. Films were applied with varying wet film thickness such that the dried films of all the compositions had thickness of approximately 1.0 mil. The films were allowed to cure at ambient conditions (25°C and relative humidity of approximately 45%) for at least 168 hours before tests for mechanical and chemical properties were carried out.

Compositions were tested for their pot-life by checking for the rise in their viscosity after mixing of the two components, at an interval of 30 minutes until their Gardner-Holdt viscosity was greater than T, (approximately double the initial value), at ambient temperature. Films were tested for drying-time (ASTM D 5895), pencil hardness (ASTM D 3363-92a); cross-hatch adhesion (ASTM D 4752), solvent resistance (ASTM D 5402), and impact resistance (ASTM D 2794-92). Chemical resistance of the films was studied by the 'spot-test' for 30 minutes.

The extent of cure of two-component polyurethane coating systems formulated with polyester polyol (conventional) and SOPEP with aliphatic IPDI based polyisocyanate, was compared under ambient and elevated temperature conditions using FTIR spectroscopy. The two sets of coatings were applied onto the potassium bromide pellets and their FTIR spectra were recorded (designated as 0-hr spectra). One of the pellets was then put in an oven maintained at 80°C, for 1 hr. The pellet was cooled in a desiccator and the spectrum was recorded (designated as heat cured sample). The second pellet was exposed to the ambient environment (approx 30° C and 40% RH) and their spectrum were recorded at regular interval (8 hrs). The final spectrum was recorded after 7 days of curing (designated as 7-day sample). Primarily, the isocyanate peaks in the spectrum were observed.

Results and discussion.

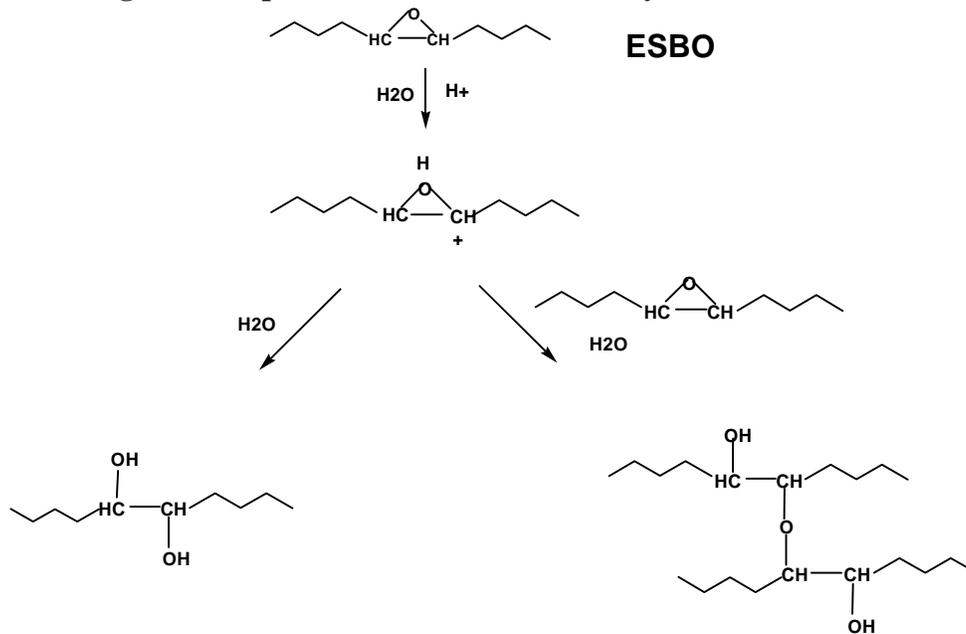
Synthesis of Polyols (SOPEPs):

The characteristics of SOPEPs prepared for the study are presented in Table 2.

The results show that it is possible to prepare SOPEP varying in hydroxyl content and viscosity by varying the amount of phosphoric acid. The values for hydroxyl contents are lower compared to the calculated values (based on each epoxide group upon hydrolysis producing two hydroxyl groups).

The acid catalyzed reaction of ESBO with water is believed to follow the reaction scheme shown in Figure 1. Under the experimental conditions used, there appears to be two competing reactions taking place simultaneously. The hydrolysis reaction, by nucleophilic attack of water on the carbon atom of the epoxide group, produces a hydroxyl on the fatty acid backbone. The other competing reaction is oligomerization by an epoxy-epoxy or hydroxy-epoxy reaction with formation of an ether linkage. Soucek, et al. have done extensive research in this area and have proposed a mechanism for oligomerization of cycloaliphatic epoxide compounds.²⁵⁻²⁶ Due to the structural similarity of ESBO with cycloaliphatic epoxide, we believe that similar reaction mechanism is probable. The lower viscosity of SOPEP-IV (prepared with 4% phosphoric acid) is believed to be due to a higher degree of hydrolysis and lower degree of oligomerization, resulting in lower average molecular weight. Lower viscosity and lower hydroxyl content for SOPEP-II can be attributed to lower degree of oligomerization due to lower epoxy content (3.5% Oxirane oxygen) of the ESBO.

Fig.1 A simplified reaction scheme for synthesis of SOPEP



It is difficult in a neat system to effect complete hydrolysis of epoxide groups before any appreciable oligomerization. Higher degrees of hydrolysis results in a product with higher hydroxyl content and lower viscosity, whereas etherification (oligomerization) results in lower hydroxyl content and higher viscosity. The process and the reagents used in synthesis of SOPEP makes them low cost polyols.

Film Properties:

SOPEP Based Compositions:

Table 5 shows ambient temperature cured film properties of PU coatings based on straight SOPEPs. For both aromatic and aliphatic systems, drying characteristics and film hardness improve as hydroxyl content of the polyol is increased. This can be attributed to increasing cross-link density of the film matrix. Physical properties of aliphatic systems are inferior to the aromatic systems. This could possibly be due to incomplete cure by aliphatic isocyanate of IPDI type used in this study²². Polyisocyanates based on IPDI have higher Tg which leads to faster setting of film resulting in incomplete cure.

Table 5. Film Properties of PU Coatings Based SOPEP

COMPOSITIONS	Ar-I	Ar-II	Ar-III	Ar-IV	Al-I	Al-II	Al-III	Al-IV
Pot-life (hrs)	9.0	9.0	6.0	5.0	12.0	12.0	9.0	7.0
Drying Time (min.)								
Surface drying	30	30	20	20	60	45	45	40
Tack-free	90	70	70	60	150	120	120	90
Pencil Hardness								
Gouge	2H	H	3H	4H	H	F	H	H
Scratch	HB	HB	H	H	HB	HB	HB	HB
Impact Resistance (D/R) (lb.inch)	160/160	160/160	160/160	160/160	60/50	160/160	80/60	120/100
Adhesion	4B	5B	4B	4B	2B	5B	5B	5B
% elongation	>32%	>32%	>32%	>32%	>32%	>32%	>32%	>32%
MEK double-rubs (Passes)	25	25	25	50	<25	25	25	25
Chemical Resistance * (Spot-test -30 min)								
Xylene	0	0	0	0	3	2	0	0
MEK	5	5	4	1	5	3	2	2
10% HCL	0	0	0	0	0	0	0	0
10% Acetic acid	0	0	0	0	0	0	0	0
10% NaOH	0	0	0	0	0	0	0	0
* 0-No marks 1-very slight marks 2- slight mark 3-prominent marks 4-partial film detachment 5-complete film detachment								

Comparison of impact resistance indicates that films of aromatic systems are significantly tougher than their aliphatic counterparts. Within the aliphatic series, impact resistance is found to improve with increasing hydroxyl content.

Results of the MEK-double rub tests indicate that, in general, PU films based on SOPEP do not have good resistance to polar solvent. That this poor solvent resistance might be due to the higher concentration of softer segments (SOPEP) in the film matrix was investigated with FTIR. The FTIR spectra for both of the 2K-PU systems, cured under different conditions are shown Figures 2-5. Based on these spectra, the following can be concluded.

1. 7-day ambient cure is equivalent to curing at 80 deg C for 1 hr.
2. Polyester polyol formulations show significantly lower degree of reaction, both at ambient and at elevated temperature, as indicated from isocyanate peak at 2258 nm (Fig.4&5). This might be due to the expected higher Tg of polyester systems leading to 'vitrification' of the film resulting in reduced mobility and reactivity of residual isocyanate and hydroxyl groups.

3. Formulations based on SOPEP show significantly higher degree of reaction at both ambient and elevated temperature curing conditions (Fig 2 & 3). This can be attributed to the greater free volume of the hyperbranched polyol structure enabling sufficient mobility of functional groups to react to a significantly higher degree compared to that for polyester polyol.

Based on the above, we believe that the poor solvent resistance (low MEK double rubs) is primarily arising from the SOPEP fatty acid chains rather than due to insufficient degree of curing.

We also observed similar results, in a separate study, for coatings based on SOPEP cured with melamine type cross-linker at elevated temperature. While all films are found to be resistant to acids and alkali, they are sensitive to polar solvent MEK, but fairly resistant to xylene.

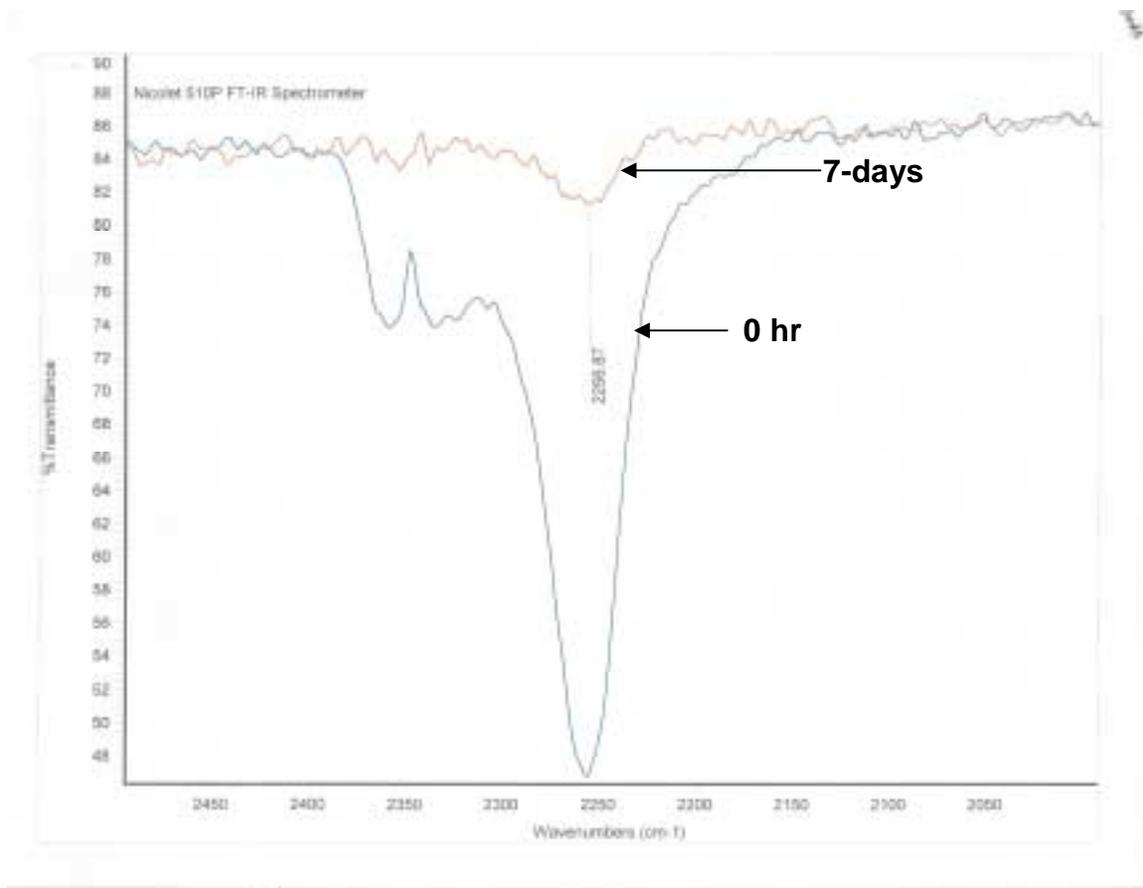


Figure 2. IPDI-SOPEP Ambient Cured Systems

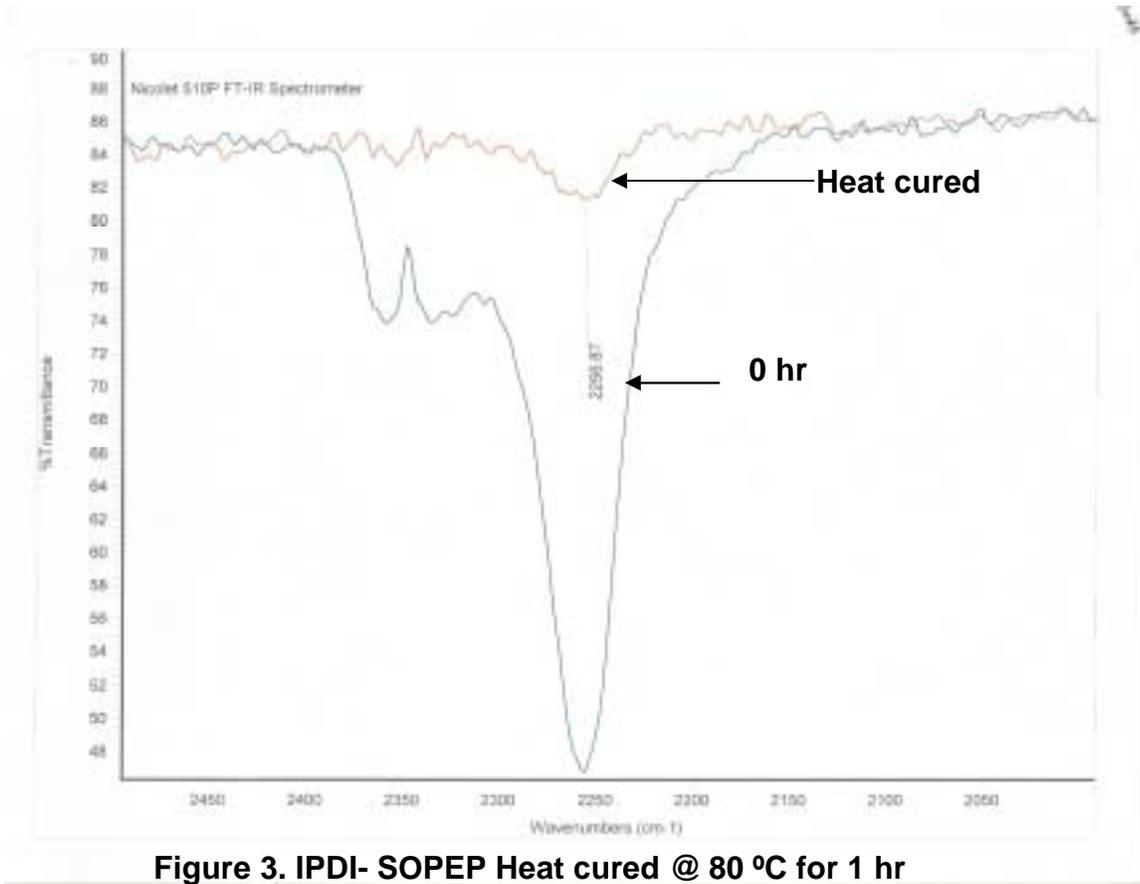


Figure 3. IPDI- SOPEP Heat cured @ 80 °C for 1 hr

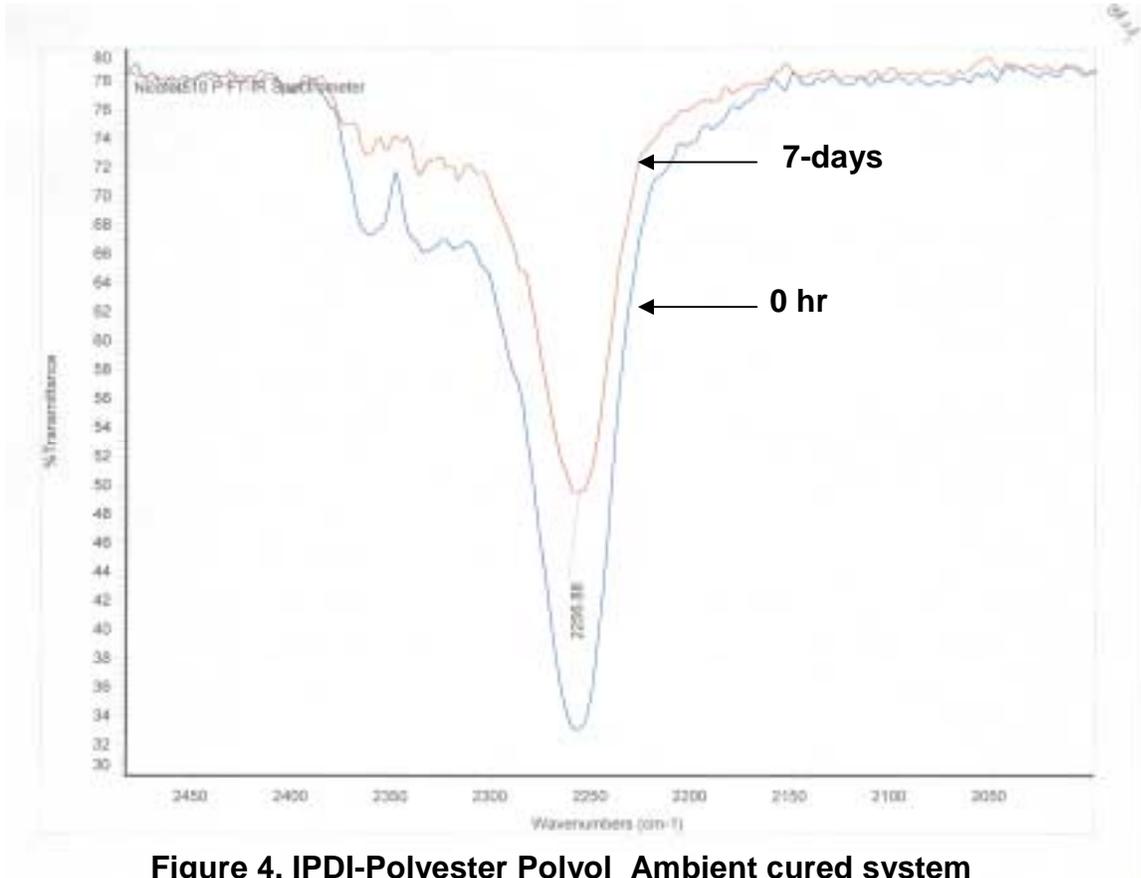


Figure 4. IPDI-Polyester Polyol Ambient cured system

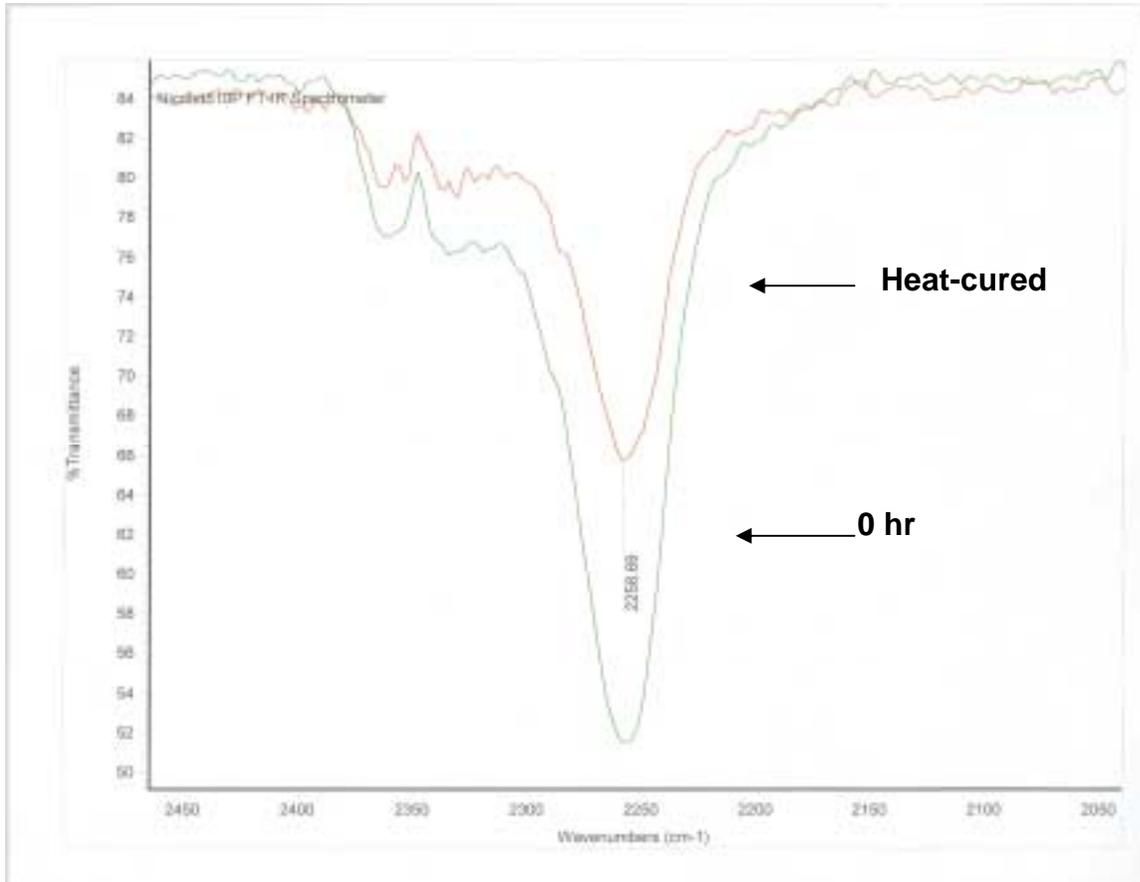


Figure 5. IPDI-Polyester Polyol Heat cured 80° C for 1 hr

VOC and Solid Content

The calculated VOC and non-volatile content of all the compositions studied are reported in Tables 3 and 4. Tertiary butyl acetate is a VOC exempt solvent. The study indicates that it is possible to formulate compositions having substantially lower VOC and higher solids due to low viscosities of SOPEP compared to polyester polyols. SOPEP has good solubility in tertiary butyl acetate, which allows the incorporation of this solvent in very low VOC formulations.

Polyester/SOPEP based Compositions

Results of the film properties of Polyester/SOPEP blend systems are presented in Table 6. Incorporation of SOPEP into polyester polyol would be expected to reduce the film hardness and solvent resistance (MEK) of the cured film, for both aromatic and aliphatic systems. However, it is evident that incorporation of SOPEP at 25% level does not significantly affect most film

properties when compared with straight polyester based films. It therefore follows that SOPEP having hydroxyl content comparable to that of polyester polyol can be incorporated up to 25% of polyester polyol without any significant loss of properties. This can result in substantial reduction in cost and VOC with increased non-volatile content at application viscosity.

Table 6. Film Properties of PU Coatings Based on SOPEP/Polyester Blends

Compositions	PS-25-Ar	PS-50-Ar	PS-75-Ar	PS-100-Ar	PS-25-Al	PS-50-Al	PS-75-Al	PS-100-Al
Pot-life (hrs)	5.0	4.5	4.5	4.5	7.0	7.0	6.5	6.0
Drying Time								
Surface drying	20	20	15	15	35	30	30	25
Tack-free	50	50	45	45	90	80	70	70
Pencil Hardness								
Gauge	3H	4H	5H	5H	H	2H	2H	3H
Scratch	H	2H	3H	3H	F	F	H	H
Impact Resistnce (D/R) (lb.inch)	160/160	160/160	160/160	160/160	130/100	140/120	160/160	160/160
Adhesion	4B	5B	5B	5B	5B	5B	5B	5B
% elongation	>32%	>32%	>32%	>32%	>32%	>32%	>32%	>32%
MEK double rubs (Passes)	25	75	200	>200	25	75	200	>200
Chemical Resistance * (Spot-test -30 min)								
Xylene	0	0	0	0	2	2	1	0
MEK	2	2	2	1	5	4	0	2
10% HCL	0	0	0	0	0	0	0	0
10% Acetic acid	0	0	0	0	0	0	0	0
10% NaOH	0	0	0	0	0	0	0	0

* 0-No marks 1-very slight marks 2-slight marks 3-prominent marks 4-partial film detachment 5-complete film detach

Conclusion

Soy-based polyols with varying hydroxyl content and viscosity can be synthesized from epoxidized soybean oil. SOPEPs can be employed as hydroxyl component of 2K-PU coating system with distinct advantages of low cost and lower VOC. Generally, hardness and solvent resistance are reduced by SOPEP systems, as compared to conventional polyester polyol based system. However, SOPEP having higher hydroxyl content can be used as reactive diluent for polyester polyols up to 25%, without any appreciable compromise in film properties. This can result in substantial reduction in VOC and cost of the coating systems.

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SUMMARY OF TASK RESULTS

Task 1: Evaluation by Paint Companies and Resin Companies

Precision Coatings tested POLYOL3.5 from Texas State University (TXSTATE) labs for low VOC waterborne coatings in December 2002 and requested more sample. An additional quart was supplied by TXSTATE in January 2003. A five gallon sample was requested from Arkema. Arkema made a run using the Texas State procedure. Arkema had a problem with the t-Butyl alcohol flash point and wanted to use Dowanol DB instead. They also had trouble removing all the solvent and wanted know how much solvent they could leave in the resin. Texas State worked with Precision Coatings to decide on a formulation with 5% Dowanol DB in the SOPEP3.5. A one gallon sample of the new formulation was sent to Precision Coatings. Performance was acceptable and a 5 gallon sample was requested in early July 2003.

Arkema made a pilot run of the SOPEP3.5 containing 5% DB. Texas State evaluated the sample in September. The product had the same specifications, but the performance was different than that of the lab sample. Texas State and Arkema collaborated on investigating the chemistry and decided that the problem was in the solvent removal stage. The pilot process was longer and hotter than the lab process causing transesterification and polymerization reactions to occur. Different process conditions and different levels of solvent left in the resin caused viscosity and performance variations. Arkema then produced another SOPEP3.5, being careful to use repeatable procedures. Texas State evaluated the product in October. The specifications of the five gallon sample of SOPEP3.5 were good, but the performance was not the same as the lab sample Precision Coatings qualified. Texas State showed that the same coating performance could be obtained with minor formulation/bake variations. Bill Murray agreed that the variations were acceptable and within the parameters of the intended use. Arkema sent the five gallon sample to Precision Coatings in late October, 2003. Precision Coatings experienced research/development delays 2004 and in 2005.

A new opportunity emerged with **Cognis Corporation** on POLYOL3.5. Massingill visited their labs and presented the results on POLYOL3.5 to a group of 10 scientists on March 13, 2003. A **The Dow Chemical Company** contacted us and scheduled a telephone conference call in March, 2003 re: POLYOL because of one of my presentations at a conference. They committed to taking the information back to their management and get back to us. Dow bought Union Carbide which is a major producer of epoxidized vegetable oils. Dow also has extensive background in the phosphate ester technology. They could easily implement this technology.

Cook, Composites, and Polymers (CCP) evaluated POLYOL lab samples in a high solids polyester baking enamel as a reactive diluent. They found that the POLYOL modification:

- lessens the amount of yellowing that occurs with QUV testing
- It appears to hurt the gloss retention
- was slower in cure response with the polyester formulation
 - needs +25°C higher cure to develop physical properties and salt spray resistance

A presentation was made to **Rohm & Haas** personnel at Springhouse, PA. A sample was requested and they agreed to a demonstration project with a California customer if the product performed well in their evaluations. R&H evaluated POLYOL as a low VOC coalescent (it did not lower the Minimum Film Forming Temperature) and as a pigment dispersant (with out much success).

Niemann & Associates (Arizona) received samples of POLYOL1.0 and 3.5. NA requested a drum of POLYOL from Arkema, but Arkema was not able to deliver for months. The customer Demonstration was canceled as NA went forward with a competitive product.

Sherwin-Williams (Chicago) and **National Ink** (Santee, CA) evaluated samples of POLYOL for water-based coatings and ink.

Dunn-Edwards (Los Angeles) wanted an ambient cured POLYOL formulation, but the moisture cured POLYOL polyurethane formulation had low MEK solvent resistance.

Kaneda Company, Ltd. of Tokyo, Japan contacted us re: POLYOL and were referred to Arkema for the POLYOL1.0 sample. An inquiry into their interests was made, but not really answered.

Task 2. Polyol Modification

Molecular weight modifications/control were the primary target during this portion of the project, as the process needed to be modified to give the desired molecular weight resin at Arkema. A new solvent process was transferred to Arkema in late January, 2003.

Work on building molecular weight by reacting aromatic acid and fatty acids with epoxidized soybean oil and various catalysts were investigated in an effort to avoid using a solvent in the process. Mixing POLYOL, acid catalyst, and epoxidized soybean oil followed by dispersing the mixed oils and then heating to 95°C lead only to modest molecular weight gains due to hydrolysis of the glyceryl ester bond at this temperature.

Task 3: POLYOL Scale-up by Arkema

Mohammad Kazemizadeh, epoxy oil research manager, and Chuck Castley, epoxy oils marketing manager, from Arkema visited TXSTATE on January 28, 2003 to discuss the soy polyol project and TXSTATE intellectual property with respect to soy polyol. Arkema reiterated its commitment to work with TXSTATE to supply pilot quantities of soy polyol for the industry evaluations. TXSTATE supplied a procedure to Arkema for making the Polyol3.5 on February 7, 2003. The viscosity of the sample they prepared was higher than anticipated. We worked on adjusting the procedure with Arkema.

Task 4. Polyol Modification to Improve compatibility

Work on controlling molecular weight by reacting epoxidized soybean oil and various catalysts was conducted in an effort to avoid using a solvent in the process. Addition of benzoic acid before phosphorylation and hydrolysis gives a POLYOL with aromatic content and improved compatibility with commercial short oil alkyd resins.

Task 6: Verification of POLYOL Quality/Performance

Bill Murray at **Precision Coatings** tested the new corrosion resistant POLYOL3.5 for low VOC waterborne maintenance coatings from Texas State labs in December 2002 and requested more sample. An additional quart was supplied by Texas State in January 2003. A five gallon sample was requested from Arkema in February 2003.

Arkema produced SOPEP3.5 using the Texas State procedure. They had a problem with the t-butyl alcohol flash point and wanted to use Dowanol DB instead. They also had trouble with viscosity and wanted to know how much solvent they could leave in the resin. Texas State worked with Precision Coatings to decide on a formulation with 5% Dowanol DB left in the SOPEP3.5. A one gallon sample of the new formulation was sent to Precision Coatings in July 2003. Performance was acceptable and a 5 gallon sample was requested in early July.

Arkema made a pilot run of the SOPEP3.5 containing 5% DB. Texas State evaluated the sample in September. The product had the same specifications, but the performance was different than that of the lab sample. Texas State and Arkema collaborated on investigating the chemistry and decided that the problem was in the solvent removal stage. The pilot process was longer and hotter than the lab process causing transesterification and polymerization reactions to occur. Different process conditions and different levels of solvent left in the resin caused viscosity and performance variations. Arkema then produced another SOPEP3.5, being careful to use repeatable procedures. Texas State evaluated the product in October. The specifications of the five gallon sample of SOPEP3.5 were good, but the performance was not the same as the lab sample Precision Coatings qualified. Texas State showed that the same coating performance could be obtained with minor formulation/bake variations. Bill Murray agreed that the variations were acceptable and within the parameters of the intended use. Arkema sent the five gallon sample to Precision Coatings.

Task 7: Prototype alkyd resin development

Addition of four moles of aromatic acid to the epoxidized soybean oil before phosphorylation and hydrolysis produced a short oil alkyd resin with low viscosity. The resin was evaluated for hardness and cure speed. The extra steps did not produce significantly better properties. POLYOL3.5 was selected as the resin of choice as a reactive diluent and as a primary resin.

Task 8: Prototype Paint Development

Prototype short oil bake coating formulations developed at Texas State were converted to prototype container coatings at Precision Coatings. Scale-up was completed at Precision Coatings after a two year delay.

Task 15: Precision Coatings Demonstration

Precision Coatings conducted a Demonstration of their new 174 g/L (1.45 lb/Gal) Low VOC POLYOL based black container coating on April 11, 2006 at a customer plant in Southern California. The current product contains 2.7 lb/Gal VOC. Five gallons of black POLYOL formulation were used to purge the paint lines and spray paint three drums on the commercial line. The three drums were flash dried, baked, cooled, and removed from the line for visual inspection and testing. Bill Murray of Precision Coatings commented that the drum coatings had good flow, good gloss, good adhesion, and good MEK solvent resistance. The drums had some streaking, possibly due to inadequate wetting. This occurred last year on start-up with the regular coatings and was corrected by reformulation. Another run was scheduled for April 12 to continue the evaluation. Precision Coatings intends to reformulate to correct the streaking and then commercialize the coatings.

Figure 15-1.

First POLYOL coated black drum exiting oven.



Figure 15-2.

Test Drums Just Off Assembly Line



Task 16: Dunn-Edwards/Sherwin-Williams/Niemann & Associates/National Ink/Valspar Demonstrations

The paper on the use of soy polyol in polyurethane ambient cured coatings was sent to Dunn-Edwards and Niemann & Associates. Proto-type paint development was stopped by poor solvent

resistance of the ambient cured soy polyol based polyurethane coatings. Several demonstrations were stopped by the high price quote from Arkema.

Figure 15-3. Test Drums Being Checked Offline



Task 17- Data Reduction, Paper Preparation, Presentations, Reports

The following presentations on POLYOL preparation and use in short oil alkyd coatings and in polyurethane coatings for wood were made:

1. Vijay M Mannari and John L Massingill, Jr, "Hyperbranched Soy Alkyd Resins For Low Voc Industrial Coatings", Proceedings of the 29th International Waterborne, High-Solids, & Powder Coatings Symp., New Orleans, Feb. 2002.
2. Vijay M Mannari and John L Massingill, Jr., "Two-Component High-Solids Polyurethane Coating Systems Based On 'Soy-Polyol', Proceedings of the 29th International Waterborne, High-Solids, & Powder Coatings Symp., New Orleans, Feb. 2002.
3. "Bio-Based Hyperbranched Polyols and Polymers", PMSE Division, National Meeting of the Amer. Chem. Soc., April, 2002.
4. V. M. Mannari, Y. Guo, Z. Chen, and J. L. Massingill, Jr., "Epoxy Acid Phosphate Esters- Dispersibility And Salt Fog Resistance", Proceedings of the 30th International Waterborne, High-Solids, & Powder Coatings Symp., New Orleans, Feb. 2003.
5. Vijaykumar Mannari, Yinzong Guo, and John L. Massingill, Jr., "Dispersibility of phosphated bio-based hyperbranched polyols", 225th ACS National Meeting, Polymer Division, New Orleans, LA, March 2003.
- A. Iyer, J. Massingill, "Soy-Oil Based Tackifiers and Adhesives", 96th AOCs Annual Meeting, Salt Lake City, UT, May, 2005.

The following paper has been published:

Vijay M. Mannari and John L. Massingill, Jr., "Two-Component High-Solid Polyurethane Coating Systems Based on Soy Polyols", JCT Research, 3(2), 151-158 (2006).

The following papers have been written/submitted for publication:

1. Yinzong Guo, Vijay M. Mannari, Pulin Patel, and John L. Massingill Jr., "Self-Emulsifiable Soybean Oil Phosphate Ester Polyols for Low VOC Corrosion Resistant Coatings", submitted JCT Research.
2. A paper entitled "Hydrolysis of Epoxidized Soybean Oil" is being revised for submission to the Journal of the American Oil Chemists Society.