A *New* Soybean Oil-ba

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The objective of this study was to develop a
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based Reactive Diluent

FOR LOW-VOC SOLVENTBORNE

Wood Stains

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Solventborne coatings are facing increasingly strict volatile organic compound (VOC) regulations. It is a challenge to reduce their VOC contents while maintaining their low cost and high performance. In this study, we have developed a low-cost, soybean oil-based reactive diluent that can significantly reduce the VOC contents of solventborne air-drying alkyd wood stains. The reactive diluent was synthesized by a two-step process. A soy intermediate composed of a mixture of mono-hydroxyl functional soy derivatives was first prepared by reacting soybean oil with mono-hydroxyl functional amines such as ethanolamine. The structure and composition of the soy intermediate were characterized with Fourier transform infrared spectroscopy and ^{1}H nuclear magnetic resonance. A star-branched reactive diluent was then obtained by reacting a multifunctional core molecule with the soy intermediate and a polyol. The reactive diluent was formulated into 250 g/L VOC wood stains in combination with a fast-drying alkyd resin to evaluate its effect on the drying performance of the stains. A 550 g/L VOC wood stain formula based on the same fast-drying alkyd resin and a 250 g/L VOC wood stain formula based on a 100% solid alkyd resin were used as the controls. The results revealed that the reactive diluent-based, low-VOC stains have comparable or better drying performance over the controls. In addition, it was observed that the reactive diluent not only improves the stability of the pigments in the stains but also enhances the penetration of the stains into the wood substrates. The reactive diluent is an effective grinding and dispersing medium for inorganic pigments in preparing zero-VOC tinting paste.

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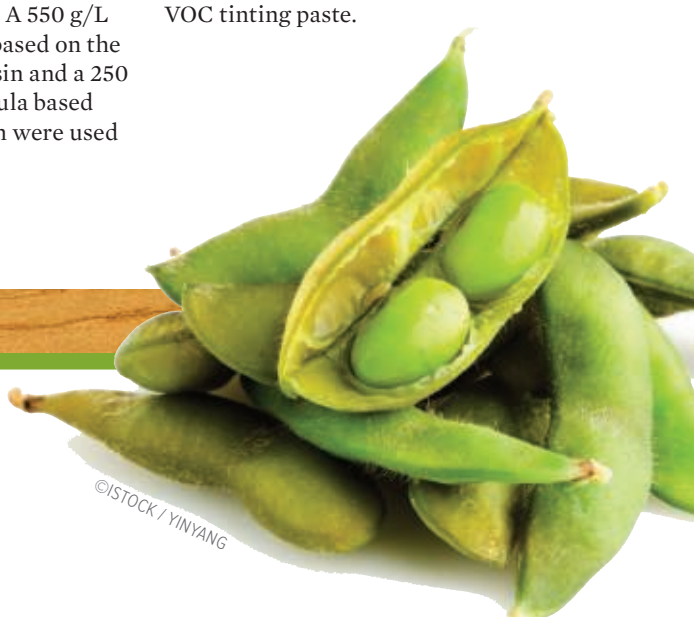
a low-cost and high performance reactive diluent based on soybean oil for solvent-based, high-solid alkyd wood stains.



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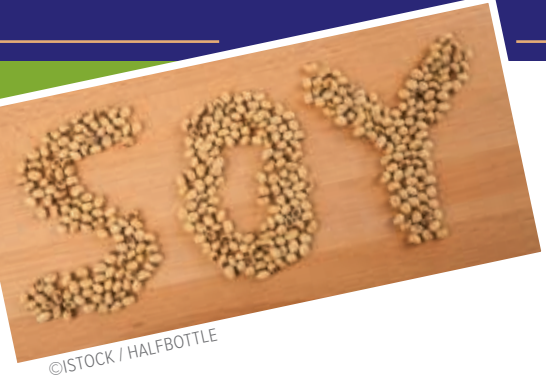

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A *New* Soybean Oil-based Reactive Diluent

INTRODUCTION

Alkyd resins have been used as coating binders in the paint and coatings industry since the 1930s. Due to their cost efficiency and versatility, excellent adhesion, and good gloss retention and corrosion resistance, alkyd resins have been used in many solvent-based coating systems. However, solvent-based alkyd coatings contribute to volatile organic compound (VOC) emissions, which usually have adverse effects on human health and the environment. With increasingly stringent VOC regulations, the coatings industry faces ever-greater pressure to reduce the VOC content in solvent-based coatings to meet these regulations. Due to their high VOC contents, solvent-based alkyd coatings have been losing their market share to other competing technologies, such as waterborne, powder, and UV-curable coatings. To regain the market share of solvent-based alkyd coatings, it is critical to lower their VOC levels to meet the strict VOC requirements and, at the same time, maintain outstanding performance.

A common approach to lower VOC content in solvent-based alkyd coatings is to use exempt solvents, such as acetone, methyl acetate, parachlorobenzotrifluoride (PCBTF), octamethylcyclotetrasiloxane (D4 cyclic siloxane), and tert-butyl acetate. However, using exempt solvents to replace conventional solvents in alkyds is limited by their odor, cost, or flammability. Another common method is to develop high-solid coatings. Although some high-solid alkyd resins with solid contents higher than 85 wt% have been developed through such methods as lowering their molecular weights, narrowing their molecular weight distribution, reducing the number of polar groups, and/or lowering their glass transition temperatures, decreased performance with these resins, such as longer drying time and softer films, has been observed.[1,2]

One appealing way to achieve high-solid alkyd coatings is using reactive diluents. Reactive diluents not only can serve as solvents to lower the viscosity of the formulation but also can be converted into an integral part of the film by taking part in the oxidative crosslinking curing process. An ideal reactive diluent should have low viscosity, low volatility, light color, good storage stability, no influence on drying times with comparable curing speed to alkyd resins, no toxic degradation products, no influence on film hardness, good through-drying, no influence on gloss, durability, etc., and is an economical replacement for regular solvents.[3] Reactive diluents for alkyd systems are also prepared preferably from seed oils, not only for sustainability and environmental considerations, but also because many seed oils have intrinsic carbon–carbon double bonds that can undergo oxidative curing and have good compatibility with alkyd resins. However, it is difficult to achieve satisfying performance in solvent-based alkyd coatings by using unmodified seed oils as reactive diluents due to the low curing rate of seed oils.[1] Although extensive research has been conducted to modify seed oils to improve their performance as reactive diluents for alkyd systems, the cost increase associated with using more expensive drying oils, such as linseed oil and tung oil as the raw materials, the involvement of multistep processes including the necessity of separation and purification, and the introduction of new issues such as storage stability and possible generation of toxic byproducts from decomposition hinder their commercial success.[4-13]

TABLE 1—Alkyd Formulations for Performance Tests

COMPOSITION	SOY FORMULA 250 VOC	CONTROL A 550 VOC	CONTROL B 250 VOC
FAST-DRYING ALKYD	32	29	0
100 WT % SOLID ALKYD	0	0	46
SOY REACTIVE DILUENT	30	0	0
ADDITIONAL SOLVENT (MINERAL SPIRITS)	0	30	15
RHEOLOGY ADDITIVE	0	2	0
DRYERS	2	2	2
WETTING AGENT	0	1	1
TINTING PASTE	36	36	36
TOTAL	100	100	100

TABLE 2—Recipes for the Tinting Pastes

COMPOSITION	OLD TINTING PASTE	NEW TINTING PASTE
HIGH SOLID ALKYD RESIN	26	0
SOY REACTIVE DILUENT	NO	41
ADDITIONAL SOLVENT (MINERAL SPIRITS)	12	0
RHEOLOGY ADDITIVE	1.7	0
WETTING AND DISPERSING AGENT	1.3	0
BURNT SIENNAS 320BS IRON OXIDE	59	59
TOTAL	100	100

The objective of this study was to develop a low-cost, soybean oil-based reactive diluent that can significantly reduce the VOC contents of solvent-based air-drying alkyd wood stains without reducing the performance of the stains. The soy-based reactive diluent was synthesized via a simple two-step process. Soybean oil was first converted to a mixture of mono-hydroxyl functional soy derivatives. The reactive diluent was then formed by reacting the soy derivatives and a polyol crosslinker with a core molecule having multiple hydroxyl-reactive groups. The star-branched structure of the reactive diluent allows the reactive diluent to bear a large number of unsaturated fatty acid chains to increase the reactive sites without significantly increasing its viscosity. The performance of the new reactive diluent was evaluated in a 250 g/L VOC alkyd wood stain that was formulated by replacing part of the mineral spirit solvent in a 550 g/L VOC alkyd wood stain with the reactive diluent. The reactive diluent-based 250 g/L VOC wood stain was also compared with a 250 g/L VOC wood stain based on a 100% solid alkyd resin. In addition, the capability of the reactive diluent in dispersing inorganic pigments to prepare tinting pastes was evaluated.

EXPERIMENTAL

Synthesis of Soy-based Reactive Diluent

The soy-based reactive diluent was synthesized via a two-step process. In the first step, soybean oil and ethanolamine were added into a 1000 ml three-neck round bottom flask equipped with an inert gas inlet, a thermocouple, a reflux condenser and a magnetic stirrer. The mixture was heated to 110°C under magnetic stirring and nitrogen purging and kept for about four hours. The reaction product was cooled to room temperature and characterized by Fourier transform infrared spectroscopy (FTIR) and ^{1}H nuclear magnetic resonance (^{1}H NMR).

In the second step, glycerol and a core molecule having multiple hydroxyl-reactive groups were charged to the flask to mix with the reaction product from the first step. The mixture was then heated to 120°C under magnetic stirring and nitrogen purging and kept for another two hours. The completion of the reaction was monitored by FTIR.

Coating Formulation

Three wood stains were formulated based on the recipes listed in *Table 1* for performance tests. A commercial fast-drying soya alkyd with a solid content of 55 wt% in mineral spirits was used both in the 250 g/L VOC soy reactive dikuent-based stain (soy formula) and the 550 g/L VOC control formula (control A). The 250 g/L VOC control formula (control B) was formulated with a commercial 100 wt% solid alkyd.

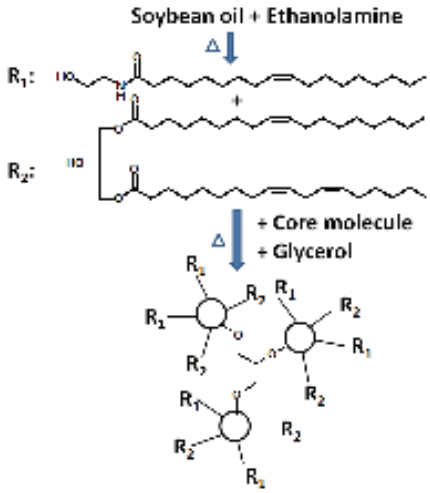
Preparation of Pigment Dispersions As Tinting Pastes

The tinting pastes were prepared based on the recipes listed in *Table 2*. The old tinting paste formula based on a high-solid alkyd resin was prepared using a horizontal mill. The new tinting paste based on the soy reactive diluent was prepared using a high-speed disperser. An iron oxide from Hoover Color (Burnt Siennas 320BS) was used in preparing the tinting pastes. All pigments were ground to a Hegman 7+ grind.

Characterization

^{1}H NMR analysis of the reaction product between soybean oil and ethanolamine was performed with an Agilent Au400 spectrometer with $CDCl_3$ as solvent and tetramethylsilane (TMS) as the internal standard. FTIR was used to monitor the synthesis process. The FTIR spectra were recorded between 4000 and 400 cm^{-1} on an IlluminatIR Infrared Microspectroscopy at a resolution of 4 cm^{-1}. Viscosity was measured using a Brookfield Viscometer (#62 spindle, 50 rpm). The finest of pigment grinding was evaluated using a Hegman gauge. A hot-box stability test was conducted at 50°C and 50% relative humidity (RH) for two months. Stain drying performance was evaluated by the following procedure. First, one coat of stain was applied to a designated area on a wood panel with a clean lint-free rag. The stain was allowed to penetrate for five minutes, after which excess stain was removed by wiping with a clean rag. The stain was allowed to dry at room temperature for one hour. Then, a clear solventborne urethane topcoat was applied with a brush. The drying performance of the stain was evaluated by examining the bleaching of the pigments in the stain layer from the stained area to the unstained area on the wood panel. Stain penetration evaluation was performed by first placing a drop of wood stain on a wood panel. After in contact for 30 minutes, excess stain was removed with a clean rag, and the stain contacted area was examined. All the performance tests were rated on a five-point scale (1 = poor, 2 = fair, 3 = good, 4 = very good, 5 = excellent).

FIGURE 1— Reaction route of the soy-based reactive diluent.



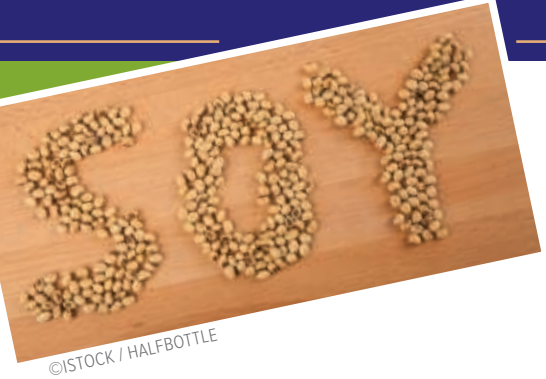


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FIGURE 2—FTIR spectra of (a) soybean oil and reaction product of soybean oil and ethanolamine at different reaction times: (b) 1 h, (c) 2 h, and (d) 3 h.

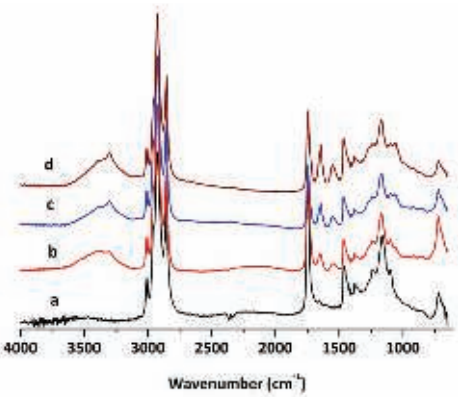
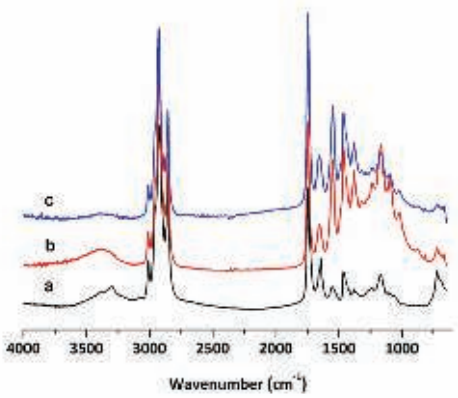


FIGURE 4—FTIR spectra of the reaction product of soybean oil and ethanolamine at different reaction times: (a) 0 h, (b) 1 h, and (c) 2 h.

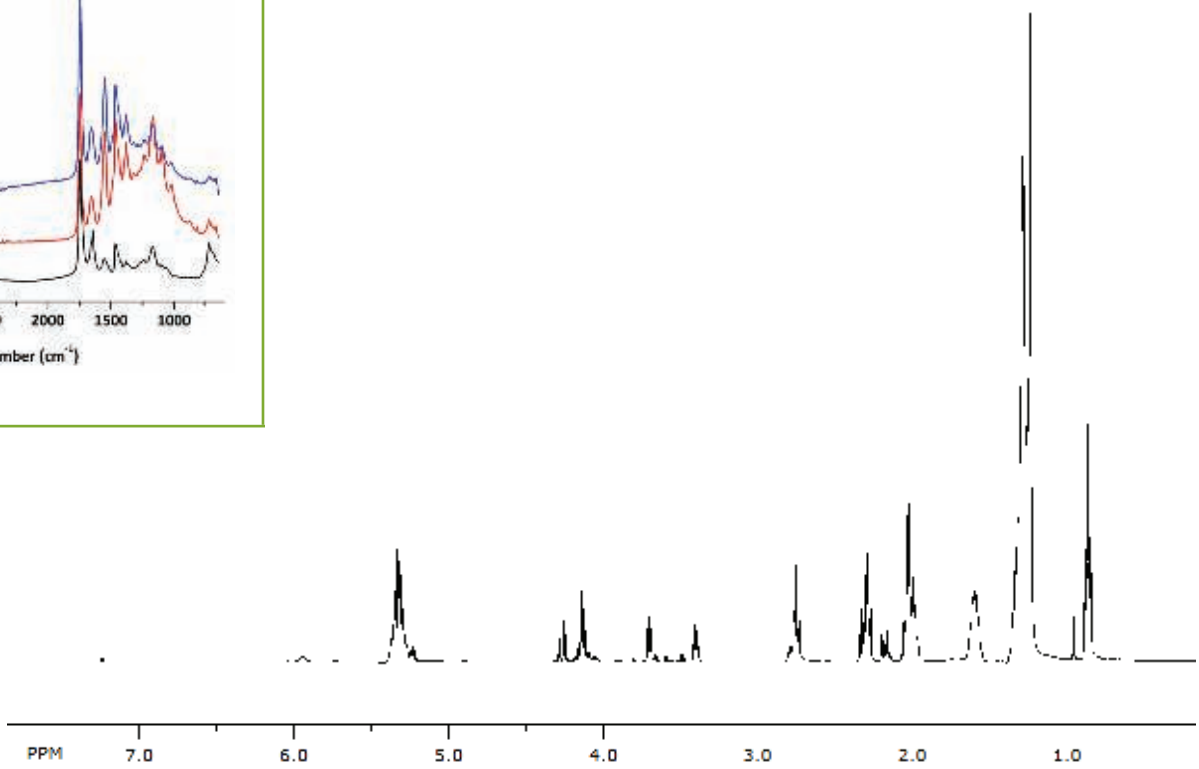


RESULTS AND DISCUSSION

The objective of this study was to develop a low-cost and high performance reactive diluent based on soybean oil for solvent-based, high-solid alkyd wood stains. Soybean oil has a very low oxidative curing rate due to the lack of reactive conjugated double bonds in its molecular structure. Our approach to enhance the curing performance of soybean oil was to increase the reactive sites by converting soybean oil into a star-branched structure, as illustrated in *Figure 1*.

In the first step, soybean oil was converted into mono hydroxyl functional soy derivatives through the aminolysis reaction with ethanolamine. Aminolysis of soybean oil to produce fatty acid amide is well known. In this article, the molar ratio of ethanolamine to soybean oil was adjusted to about 1:1 in the aminolysis reaction so that one soybean oil molecule could be converted into one fatty ethanolamide and one diglyceride, both of which have only one hydroxyl group. The reaction was monitored with FTIR and hydroxyl value and amine value titration. The titration results demonstrate that the reaction was close to complete in three to four hours, because there was no obvious change in the amine value or hydroxyl value after three hours of reaction. *Figure 2* shows the FTIR spectra of soybean oil and reaction product of soybean oil and ethanolamine at different reaction times. The appearance

FIGURE 3—^{1}H NMR spectra of the reaction product between soybean oil and ethanolamine.



of the –OH band at 3300–3400 cm^{-1} and carbonyl amide band at 1640 cm^{-1} and diminishing of the carbonyl ester band at 1740 cm^{-1} confirmed the formation of fatty acid ethanolamide.

The ^{1}H NMR spectral data of the reaction product between soybean oil and ethanolamine in *Figure 3* also confirmed the formation of fatty acid ethanolamide: δ 0.86 (–CH_3), 0.95 (–CH_3 of n-3 polyunsaturated fatty acids), 1.25 (–CH_2–), 1.59 (–CH_2–CH_2–COO–), 2.01 (–CH_2–CH=CH–CH_2–), 2.17 (–CH_2–CO–NH–), 2.30 (–CH_2–COO–), 2.74 (–CH=CH–CH_2–CH=CH–), 3.40 (–NH–CH_2–CH_2–OH), 3.69 (–NH–CH_2–CH_2–OH), 4.13 and 4.27 (–O–CH_2–CH(–O–)–CH_2–O–), 5.24 (–O–CH_2–CH(–O)–CH_2–O–), 5.32 (–CH=CH–), 5.94 (CO–NH–).

The conversion of the reaction in the second step to obtain the final product can be easily monitored with FTIR. As shown in *Figure 4,* the gradual diminishing of the –OH band at 3300–3400 cm^{-1} with increasing reaction time confirmed the gradual conversion and completion of the reaction. The disappearance of the –OH peak at 3300–3400 cm^{-1} in *Figure 4c* indicates that the second step reaction could be finished in about two hours. The final product has a Brookfield viscosity of 150 centipoise (cp). In comparison, the Brookfield viscosity of soybean oil is 50 cp. The new reactive diluent also has 83 wt% of soy content.

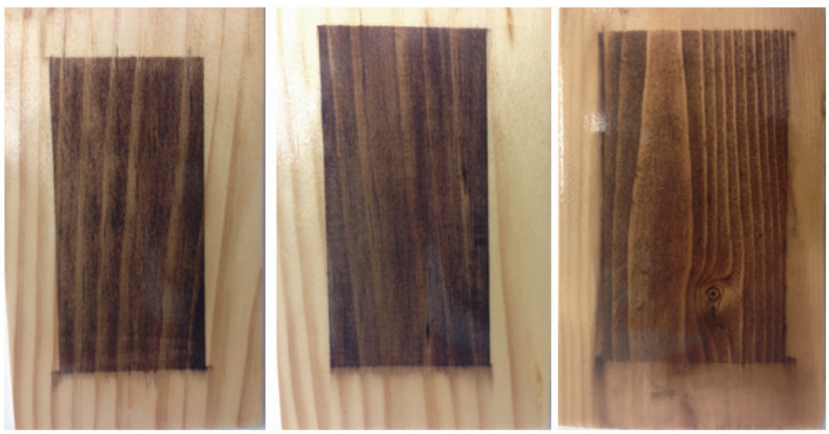
The performance of the soy-reactive diluent-based stain and the control stains in terms of drying performance, hot-box stability, and pigment penetration is listed in *Table 3*. The drying performance of the three stains was evaluated by examining the bleaching of the stains when a topcoat was applied after the stains had been dried for a certain time. The left and middle coated panels in *Figure 5* correspond to the 250 VOC soy-reactive diluent-modified stain and the original 550 VOC stain respectively. The negligible pigment bleaching on these two panels indicate that both stains can dry in one hour at room temperature. The result demonstrates that the incorporation of the soy reactive diluent more than 30 wt% of the total formula did not affect the drying performance of the stain. In comparison, the 250 VOC formula based on a 100 wt% solid alkyd showed inferior drying performance. There was still significant bleaching of pigments even after three hours of drying when a topcoat was applied, as shown on the right panel in *Figure 5*. The stain penetration evaluation comparison between the 250 VOC soy formula and the 550 VOC control formula is illustrated in *Figure 6*. The top part in *Figure 6* shows the wetting and spreading of the wet stains, and the bottom part shows the leftover stains after excess stains were wiped off. The soy formula applied on the left side of the panels not only showed better stain penetration with deeper color but also displayed better wetting and spreading, although there was no additional wetting and dispersing agent existing in the soy formula. In terms of viscosity, the soy formula and the 250 VOC control formula both have a higher viscosity than the 550 VOC control formula. All the tested stains showed comparable hot-box stability with slight setting of pigments after two months in hot box.

The reactive diluent was also used to grind inorganic pigments to evaluate its ability as the medium in preparing tinting pastes. Two tinting pastes were prepared and evaluated based on the recipes in *Table 2*. The performance comparison of the two tinting pastes

TABLE 3—Performance Comparison of the Three Wood Stains

PERFORMANCE	SOY FORMULA 250 VOC	CONTROL A 550 VOC	CONTROL B 250 VOC
FAST DRYING	5	5	3
PIGMENT PENETRATION	5	4	–
HOT-BOX STABILITY	4	4	4
VISCOSITY (CP)	258	150	278

FIGURE 5—Stain drying performance evaluation on 250 VOC soy reactive diluent modified stain after 1 h drying (left), 550 VOC stain (control A) after 1 h drying (middle), and 250 VOC stain (control B) after 3 h drying (right).



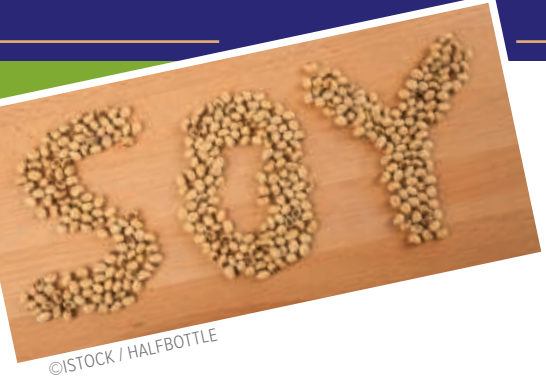


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FIGURE 6—Stain penetration evaluation: 250 VOC soy formula (left) and 550 VOC control formula (right). Excess stain was wiped off after 30 min contact.

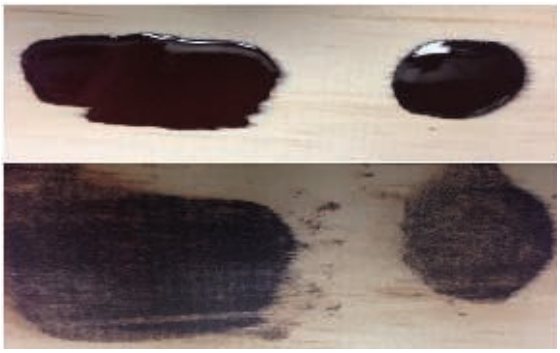

FIGURE 7—Color strength comparison between the old tinting paste (left) and the soy diluent based new tinting paste (right).

TABLE 4—Performance Comparison of the Two Tinting Pastes

PERFORMANCE	OLD TINTING PASTE	NEW TINTING PASTE
VOC (G/L)	187	0
HEGMAN READING	> 7	> 7
COLOR STRENGTH	4	5
HOT-BOX STABILITY	4	4

is listed in *Table 4*. The old tinting paste based on a high-solid alkyd was prepared by a horizontal mill and has 187 g/L VOC. Compared with the old tinting paste, the new tinting paste was prepared using a high-speed disperser with only two components, the reactive diluent, and the pigment. Although both tinting pastes have the same pigment loading and a Hegman gauge reading over 7, the new tinting paste displayed higher color strength, as shown in *Figure 7*. The new tinting paste also showed comparable hot-box stability despite the fact that no wetting and dispersing agent or rheology additive were used. Since the new tinting paste is zero VOC, it could help further lower the VOC level and provide more flexibility to the stain formulation.

CONCLUSION

We have developed a soybean oil-based reactive diluent with a star-branched structure that allows a high number of reactive sites and relatively low viscosity. The new reactive diluent has been incorporated into a 550 g/L VOC wood stain to lower its VOC to 250 g/L without affecting its fast-drying performance. The reactive diluent in the stain not only promotes wetting, spreading, and penetration of the stain on wood substrates, but also provides the stain with good storage stability without the need for any wetting and dispersing agent and rheology additive. The reactive diluent could also act as an effective medium in grinding and dispersing inorganic pigments to prepare zero-VOC tinting pastes for solvent-based alkyd wood stains.

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