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SOLVING A VOLATILE PROBLEM

New liquid polybutadiene polymer replaces solvent and improves application. By Anne-Sophie Hesry, Stacey Syron and Malcolm McInnes, Synthomer (UK) Ltd.

Reducing the level of volatile organic compounds (VOCs) in solvent-based alkyd resin systems poses a huge challenge for formulators. A novel liquid hydrocarbon polymer minimises VOCs and offers improved application properties in clear coatings. A newly developed liquid polybutadiene polymer provides hope for more eco-friendly binder systems.

Historically, the majority of coatings were solvent based, but with growing emphasis on the reduction of Volatile Organic Compounds (VOCs), such systems are under significant pressure. Where an application still demands the performance of a solvent-based coating, reduction of VOCs while maintaining critical application properties such as viscosity, has become increasingly important.

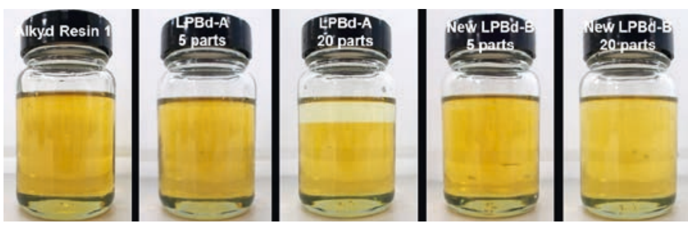
The modern coatings formulator now faces the significant challenge of minimising solvent whilst achieving an aesthetically acceptable, defect-free film at minimal cost. A common approach is to increase the solids content, but this typically results in increased product viscosity which may lead to difficulty during coating application.

Alkyd surface coatings continue to be one of the most highly consumed types of coatings globally, despite the increasing use of other polymer film formers. The success of alkyd resin systems is a result of their relatively low cost, versatility and familiarity of end users. They can be tailored to meet a variety of end-use requirements through the choice and ratio of reactants and/or modifiers. Producers continue to develop new and improved systems for high-solids formulations to meet increasingly stringent air pollution regulations.

Various alternative approaches may also be used to adjust the final coating formulation in order to lower the viscosity so that less solvent is needed to bring the paint to within the required application viscosity. Liquid polybutadienes (LPBDs) are highly reactive, liquid hydrocarbon polymers which can be formulated into solvent-free or low solvent coating formulations. These polymers are similar in many respects to natural drying oils, but due to their high level of unsaturation the cure rate of certain grades is faster than many natural oils and can be accelerated by using metal driers. In comparison with natural oils, the LPBD films are typically lighter in colour, harder and more chemically resistant. They have proven to be particularly suited to primer coat applications, exhibiting adhesion and excellent corrosion resistance on steel substrates.

Further research has been carried out into the range of potential properties delivered by incorporating LPBDs in solvent-based coatings. In

Figure 1: Storage stability of blends LPBD/Alkyd resin 1.



RESULTS AT A GLANCE

→ Alkyd surface coatings are in high demand but the properties they offer come at a cost. The emphasis on reducing VOC levels has led to the development of a novel liquid polybutadiene (LPBD).

→ A comparison of systems using a commercially available LPBD-A with those using the new LPBD-B instead of a solvent shows benefits, for example, in higher loading.

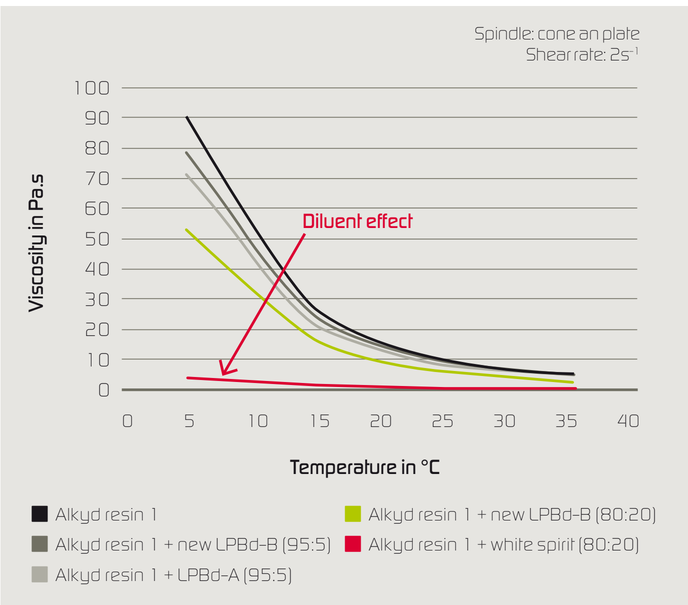
→ Application properties such as substance penetration and drying time were improved by substituting solvents with high levels of LPBD-B.

→ Reducing the quantity added may help to increase hardness.

→ Further research will explore the benefits of LPBD in other binder systems and in coatings used on different substrates.

this study we focus on the benefits delivered by incorporating a newly developed liquid polybutadiene grade (LPBD-B) in a solvent-based alkyd coating when compared to other commercially available liquid polybutadiene grades. The new LPBD-B has a lower molecular weight and higher 1,2 vinyl content than the commercial product, LPBD-A.
The results demonstrate how the next generation LPBD-B delivers improved compatibility within the resin system enabling potentially greater formulation changes and even moving closer to a solvent-free system. Our study also shows that it is possible to lower viscosity whilst simultaneously enhancing the coating's performance properties.

Figure 2: Rheology profile of modified alkyd blends.



HIGHER LOADING WITH NOVEL RESIN

Three common coating long oil alkyd-based resins were assessed; one based on linseed oil at 100% solid content, and two at 70% solids in white spirit (one based on linseed oil and one on soya oil). Blends, prepared at specific ratios, were dispersed for 5 minutes on a high speed disperser at 2000 rpm. The blends were then transferred to glass containers to assess their storage stability (*Figure 1*). One lot was left at room temperature, the other was placed in an air oven at 40°C for 24 hours. The compatibility between LPBD polymers in alkyd binder systems was assessed and a visual inspection after 24 hours and 7 days was conducted. Good compatibility was obtained in all three alkyd resins with both LPBD products.
The following study is mainly focused on work with solvent-based Alkyd resin 1 (100% long linseed oil). Its compatibility with different LPBD polymers was evaluated in detail. Following this screening, a maximum load of polymer in Alkyd resin 1 was determined. To complete the assessment, each blend was brushed on foil paper to highlight any potential film defects.
A benefit was observed from using the new LPBD-B over LPBD-A, with greater compatibility in Alkyd resin 1. A higher loading in the resin can be achieved with new LPBD-B without adverse effects on the visual

Table 1: Typical formulations example to assess drying time.

<table>
<tr><th>Formulation</th><th>B01</th><th>B02</th><th>B05</th><th>B06</th></tr>
<tr><td>Alkyd resin 1</td><td>71.5</td><td>68.1</td><td>68.0</td><td>58.3</td></tr>
<tr><td>LPBD-A</td><td>–</td><td>3.6</td><td>–</td><td>–</td></tr>
<tr><td>New LPBD-B</td><td>–</td><td>–</td><td>3.6</td><td>14.5</td></tr>
<tr><td>White spirit</td><td>25.7</td><td>25.5</td><td>25.6</td><td>24.4</td></tr>
<tr><td>Blue pigment</td><td colspan="4">0.4</td></tr>
<tr><td>Cobalt drier</td><td colspan="4">0.5</td></tr>
<tr><td>Zirconium drier</td><td colspan="4">1.6</td></tr>
<tr><td>Calcium drier</td><td colspan="4">0.3</td></tr>
<tr><td>Total (g)</td><td>100.0</td><td>100.0</td><td>100.0</td><td>100.0</td></tr>
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Figure 3: Set-up for wood penetration.

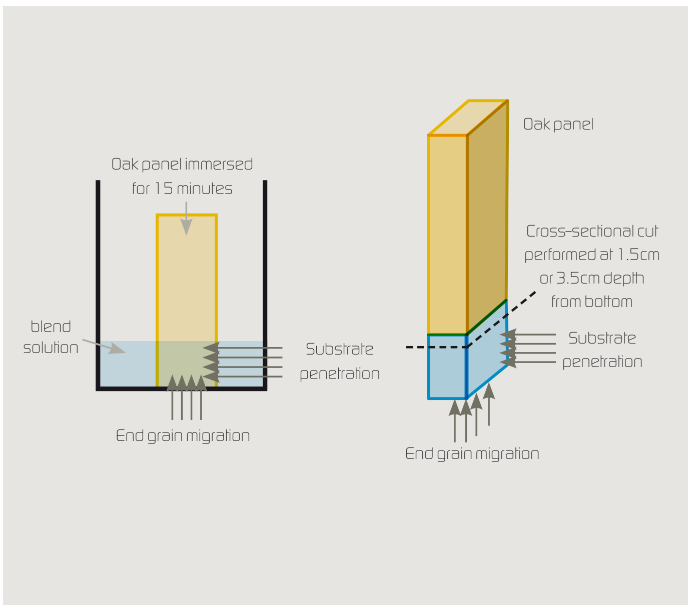
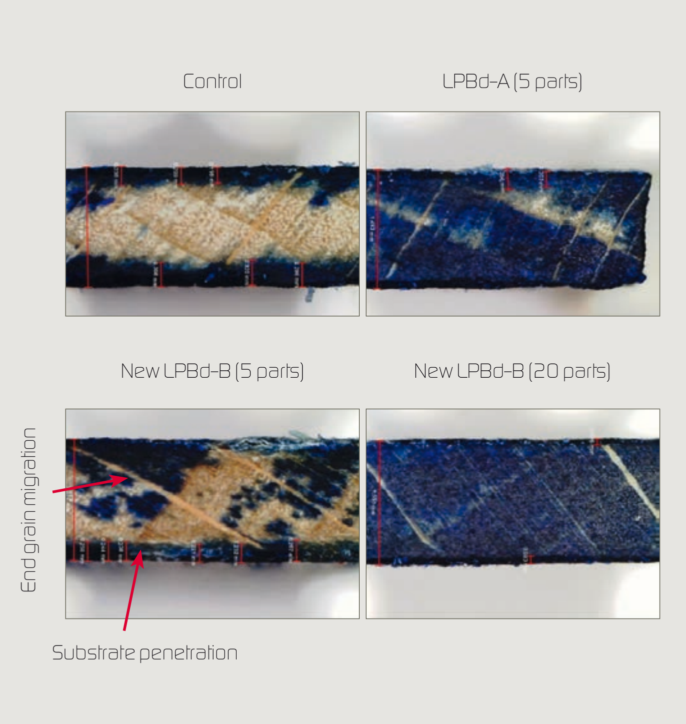


Figure 4: 1.5 cm depth cross-section of oak panels after 15 minutes dip.



aspect of the coatings. Brush out on foil paper showed no film defects in wet or dry state.

APPLICATION PROPERTIES IN CLEAR COATINGS

To evaluate the application benefits, Alkyd resin 1 was formulated in a clear coating; LPBD-A and new LPBD-B were added at different ratios. Application properties including drying time, rheology and hardness were assessed. Additional information was collected with a substrate penetration assessment and a study to move towards a 100% solid content system with lower VOC content.

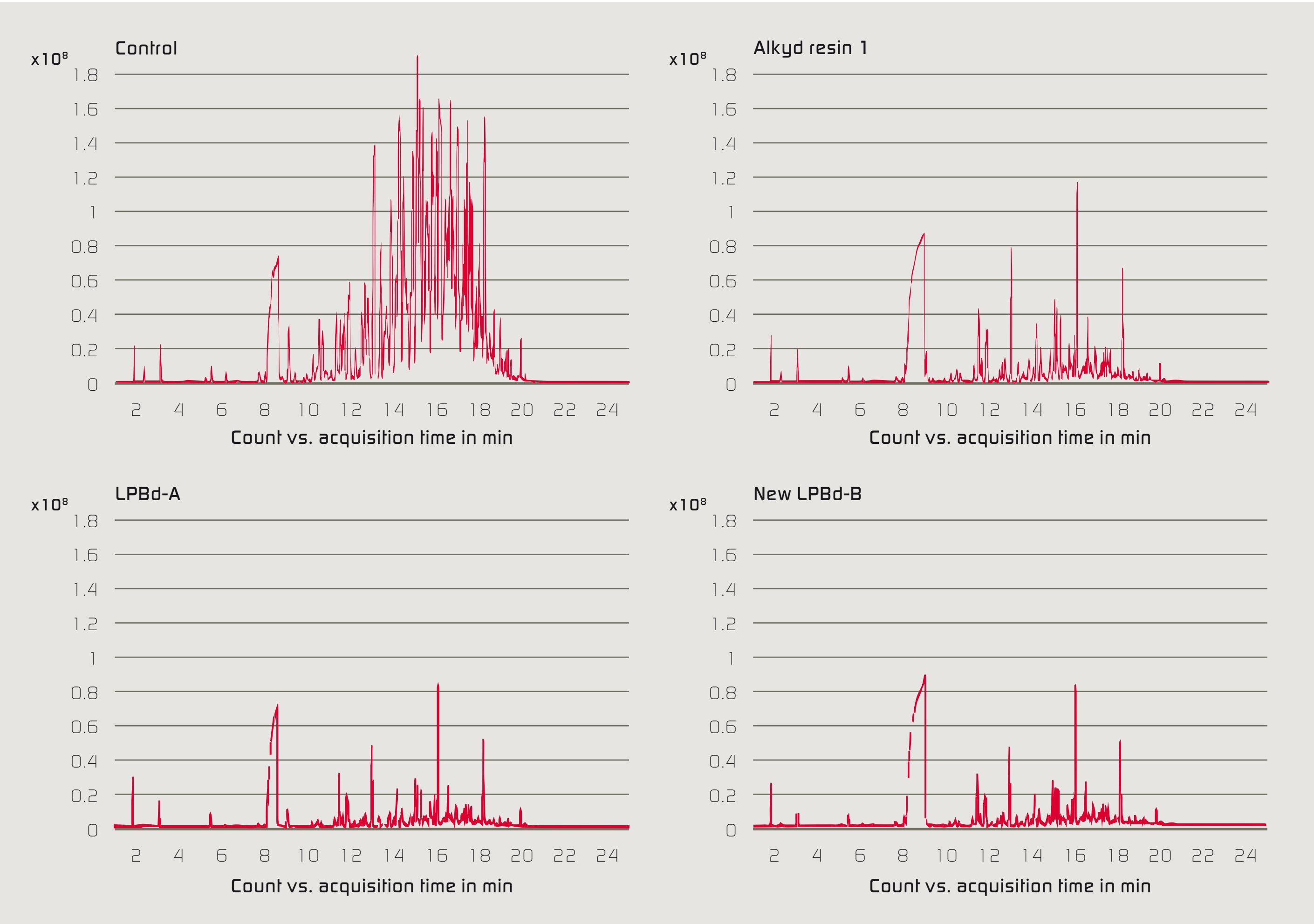
RHEOLOGY

Blend rheology profile was determined on a rheometer, see *Figure 2*. The viscosity of Alkyd resin 1 decreased as the temperature increased. Similar behaviour was obtained when adding either LPBD-A, New LPBD-B, or solvent (i.e. white spirit). A solvent-based blend (20 parts) had the greatest diluent effect on the alkyd resin.

DRYING TIME IMPROVED WITH HIGH ADDITION

A series of formulations was prepared to assess the effect of liquid polybutadiene polymers on drying time. Alkyd resin 1 was partly replaced by LPBD-A or new LPBD-B. Viscosity of each preparation was adjusted by adding white spirit to achieve an equivalent viscosity at room temperature (*Table 1*).

Figure 5: Chromatograms showing the difference in VOC content.



Each formulation was applied on glass panels at 75 µm wet film thickness. The drying time was assessed simultaneously with a linear drying time recorder. The open time and complete through cure were determined by visual assessment of the scratched surfaces of each dried coating (*Table 2*).

The open time is slightly increased by the addition of the new LPBD-B, while LPBD-A did not show significant impact compared to the control sample, containing only Alkyd resin 1.

The complete cure is very slightly increased by a low addition of LPBD-A or new LPBD-B compared to the control recipe. Significant differences were observed with high addition of new LPBD-B, giving a shorter complete cure time (*Table 3*).

SLIGHT HARDNESS INCREASE AT LOW ADDITION

To assess hardness, a series of formulations were developed by replacing parts of the Alkyd resin 1 and parts of white spirit with LPBDs. Viscosity was not adjusted to emphasise the potential benefit of LPBD.

The coating hardness was assessed using a pencil hardness method. A wet film thickness (wft) of 100 µm was applied to glass panels with a flat applicator. The coatings were allowed to dry for 7 days and 14 days prior to testing.

Adding LPBD-A in the clear coating did not present any benefits in pencil hardness. The coating was similar or lower in hardness compared to the control (no additive in Alkyd resin 1). The incorporation of new LPBD-B, allowed an increase of pencil hardness at a low-level addition. A higher addition level did not show benefit in hardness properties. It was noticed that a higher addition of LPBD tended to slightly lower the pencil hardness of the clear coating.

GREATER SUBSTANCE PENETRATION AT HIGH ADDITION

Oak panels were selected to assess substrate penetration. A series of blends were prepared with the aim of highlighting any additional potential benefits from using LPBD.

Each blend was transferred to a glass container. Oak panels were immersed for 15 minutes in the coating solution, then excess coating was removed. Each oak panel was allowed to set at ambient temperature prior to cutting a cross-section at 1.5 cm or 3.5 cm depth from the bottom of the panel. The test pieces were sanded, then digital microscopy was used to examine each cross-section. Both surface and end grain migration were evaluated. (See *Figure 3* and *4*)

According to the digital microscopy of a cross-section at 1.5 cm depth, it was found that surface substrate penetration would mostly occur within the control blend. Adding 5 parts of LPBD-A to the clear coating allowed a better coverage of the wood piece and significantly, complete end grain migration was observed. There is some evidence that adding 5 parts of new LPBD-B further improved the end grain migration compared with the control formulation. To achieve full coverage, new LPBD-B, required 20 parts addition.

A further cross-section at 3.5 cm depth was conducted to identify how blends behave more deeply into the grain of the wood. In the control specimen, substrate penetration was observed along with some end grain migration in limited areas. Adding 5 parts of LPBD-A gave a similar profile of wood penetration to the control blend but no end grain penetration was noted. Despite giving a lower wood penetration at 5 parts addition, new LPBD-B gave a similar end grain migration to the control. It was noticed that the end grain migration was present along the specimen. At 20 parts addition however, more significant wood penetration was observed with new LPBD-B compared with the control, with more significant end grain migration visible along the specimen.

HIGHER SOLIDS REDUCE VOCS

One way to reduce VOC in a solvent-based coating is to increase the solid content. A series of formulations were developed, replacing the amount of white spirit by LPBD-A, new LPBD-B, or Alkyd resin 1. This moves the recipes towards higher solids content and allowed evaluation of 100% solid content systems.

Levels of metal driers and anti-skin agent were adjusted and calculated on %w/w on total resin weight.

Each formulation was applied on a glass panel with a flat applicator at 50 µm and 100 µm wet film thickness. Coatings were allowed to dry for 24 hours at room temperature prior to observation.

To compare the different systems, a control formulation with 65% solids content was assessed, which showed good film-forming behaviour on glass at 50 µm and 100 µm. By increasing the total solids content by adding Alkyd resin 1, a good film was formed at a low thickness of 50 µm, whereas wrinkling defects were observed at 100 µm. The wrinkling effect would be most likely due to rapid surface drying. Adjusting the metal drier levels in the formulation should eliminate this defect.

Table 2: Drying time results.

	B01	B02	B05	B06
Formulation	Alkyd resin 1	Low addition of LPBD-A	Low addition of New LPBD-B	High addition of new LPBD-B
Average				
Open time (h:min)	00:15	00:15	00:30	00:45
Complete cure (h:min)	30:30	30:45	31:45	23:15

Table 3: Pencil hardness data.

	V01	V02	V03	V06	V13
Pencil hardness after 14 days	Control	Low addition LPBD-A	High addition LPBD-A	Low addition new LPBD-B	High addition new LPBD-B
100 µm wft	B	B	<B	HB	B

Order of pencil hardness

6B 5B 4B 3B 2B B HB F H 2H 3H 4H 5H 6H

Very soft ← → Very hard

"The addition levels of LPBD have been deliberately kept as low as practical to demonstrate the benefits but minimise the cost impact."

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4 questions to Anne-Sophie Hesry

Applying the Liquid Polybutadienes (LPBDs), how will costs develop? *An important part of our research in this area has been to ensure it is possible to have a cost effective finished formulation for more demanding applications. The addition levels of LPBD have been deliberately kept as low as practical to demonstrate the benefits but minimise the cost impact. Unlike solvents, the LPBds are permanently bound into the coating, so they perform multiple functions and can bring the formulator valuable technical benefits.*

The LPBDs are seen as similar to alkyds "in many respects". Where do they differ the most significantly? *The compatibilities and drying behaviour are like alkyds due to the high level of unsaturation. The LPBDs however retain their physical properties over a wide temperature range, particularly low temperatures. LPBD films are typically lighter in colour, harder and more chemically resistant. Their structure means they can also be cured by other routes such as sulphur or peroxide vulcanisation.*

Can you quantify the difference between LPBD-B and LPBD-A? *LPBDs are highly reactive, liquid hydrocarbon polymers, which can be designed with different chain length and microstructure combinations. The effect of these variants on application properties, formed part of the study detailed in our research paper.*

Is the addition of LPBD limited with regard to compatibility? *There are compatibility limits, yes, with the most stable systems achieved with long oil alkyds. However, our development work has identified key elements of the polymer design, which improves general compatibility and so offers greater formulation scope.*

Introducing LPBD-A to increase the total solids content of the clear system gave film defects at both thicknesses. This result confirmed the initial outcomes following the compatibility study i.e. at high loading, LPBD-A cannot be incorporated homogenously. Benefits were clearly noticed with the introduction of new LPBD-B, to achieve a higher solid content system. Clear transparent films were obtained with no visual defects at both thicknesses (50 µm and 100 µm).
Moreover, increasing the solids content had an impact on the viscosity of the clear systems. The diluent effect of LPBD is confirmed with reference to formulations V15 (LPBD-A) and V17 (new LPBD-B). The increase was more significant with the Alkyd Resin 1 (formulation V21), which could lead to application issues associated with the high viscosity.
To determine VOC content in those formulations, GC-MS analysis was performed according to an internal test method.
Results and chromatograms from GC-MS analysis clearly demonstrated a drop in VOC in formulations with a higher solid content. Replacing white spirit with LPBD in Alkyd resin 1, significantly reduced the amount of VOCs in the formulation. Limited differences were observed between the resins that were added to replace the solvent content, i.e. in V15, V17, and V21. (*Figure 5*)
As expected, increasing the solid content by adding polymer resins reduced the total amount of VOC. White spirit is obviously a major contributor to VOC in the formulations tested.

ONGOING RESEARCH TO EXPLORE BENEFITS IN DIFFERENT SYSTEMS

This study has confirmed benefits from use of liquid polybutadiene polymers in solvent-based coatings with additional enhancements seen from a new liquid polybutadiene. Results demonstrate that it is possible to reduce the VOC content of a solvent alkyd coating by increasing the solid content using additions of liquid polybutadiene. This 100% solids content liquid polymer type, suggests a move closer to 100% solids content is achievable. It was additionally shown that incorporating a new LPBD increased wood penetration, and end grain penetration in particular. Other advantages noted were longer open time during drying of clear systems coupled with a potential for faster through cure. The ability to harden the dry film was also possible by selecting the appropriate addition level of liquid polybutadiene.
Application properties were enhanced by using a new development liquid polybutadiene polymer, without adverse effects on other critical properties such as gloss level, colour or outdoor exposure.

We have demonstrated the benefits of a development liquid polybutadiene product in one specific binder system used in solvent-based coatings. Further work is planned to explore the use in other binder systems and evaluate performance on different critical substrates including oily, metal, and poorly prepared surfaces.