SUMITOMO CHEMICAL

High Performance Plastic

SUMIKASUPER™ LCP

Soluble LCP: VR Series

Technical Note

LIQUID CRYSTAL POLYER

01

SUMIKASUPER™ LCP Property Benefits

SUMIKASUPER liquid crystal polymers (LCPs) are a family of fully aromatic polyesters known for their broad chemical resistance[1], high-thermal stability and mechanical performance, inherent flame retardance[2], excellent electrical properties[3], and high resistance to stress cracking. This makes SUMIKASUPER LCPs ideal for use in:

- **Electrical and electronic components** (including fiberoptic cables, printed circuit boards (PCBs), chip carriers, connectors (conventional, radio-frequency (RF), and fiber-optic), and other surface-mount components);
- **Microelectromechanical systems** (MEMS);
- **Automotive parts** (including components for ignition and transmission systems, lamp sockets, pump components, coil forms, and sensors);
- **Printer/copier/fax components**;
- **Non-stick cookware**;
- **High-barrier/retort-processed food containers**; and
- **Components for chemical processing** (including pumps, meters, and valves).

High-performance LCPs are most commonly processed by injection molding, although they can be spun into fibers, extruded into sheet and film products, and converted to coatings.

For a more thorough discussion of general properties, design, and processing recommendations for SUMIKASUPER LCPs, please see https://www.sumitomo-chem.co.jp/sep/english/products/lcp/.

1 Resistance is excellent to strong and weak acids, alcohols, esters, ketones, and aromatic, chlorinated, and halogenated hydrocarbons over a broad range of temperatures. Hydrolytic stability in boiling water also is excellent. A more comprehensive treatment of the chemical resistance of LCPs is shown in Table 1 at www.sumitomo-chem.co.jp/sep/english/products/lcp/lcp_bs_kagaku.html.

2 SUMIKASUPER LCPs are considered to be flame-retardant materials and are classified as UL94 V-0. However, they should be handled and stored well away from places of heat and sources of flames. If the material catches fire, use water, foam, or chemical fire extinguishers to extinguish any flames.

3 Electrical properties include high electrical resistivity, low relative dielectric constant, and low dissipation factor.

02

SUMIKASUPER VR SERIES: World's First Soluble LCPs for High-Performance Thin Films

As noted previously, liquid crystal polymers are well-known for their broad chemical resistance. While that property is usually advantageous for molded parts, it makes converting LCPs into films very challenging, since there are few chemicals (and most of those are fluorinated aromatic solvents) in which LCPs can be dissolved in order to reduce viscosity sufficiently to apply them to metals, polymers, elastomers, glass, fabrics, and other substrates.

SUMITOMO CHEMICAL'S longstanding research focus on unique materials has led to development of the **world's first commercial product line of chemically soluble LCPs**, which we call the **SUMIKASUPER VR Series**. Supplied in the form of a liquid varnish, the products can be dissolved in a commonly available organic solvent (N-methyl-2-pyrrolidone or NMP[4]) and used to produce thin films via solvent casting[5]. In turn, these films can then be used to enhance the performance of:

- **Flexible copper-clad laminates** (CCLs) for circuit boards in mobile/smart phones, laptop computers, digital cameras, and hand-held games, etc.
- **Rigid CCLs** for circuit boards, LED lighting, LCD TVs, tablet computers, and in a variety of automotive electronic components, including power control modules.
- **Acoustical diaphragms** for speakers and headphones.

4 NMP is a good solvent that is commonly used for polyimide, polyurethane, and acrylic polymers. It does not negatively affect metal substrates, but should not be used on polyimide film substrates.

5 Prior to development of the SUMIKASUPER VR Series, the only way to produce an LCP film was by melt extrusion, since LCPs could only be dissolved in special, fluorinated aromatic solvents. However, by modifying the chemical structure of SUMIKASUPER LCP, it is now possible to dissolve VR Series products in NMP, a common organic solvent. This has made it possible to create LCP films via the solution-casting method. The resulting LCP film has low in-plane anisotropy.

03

Soluble LCPs: General Properties

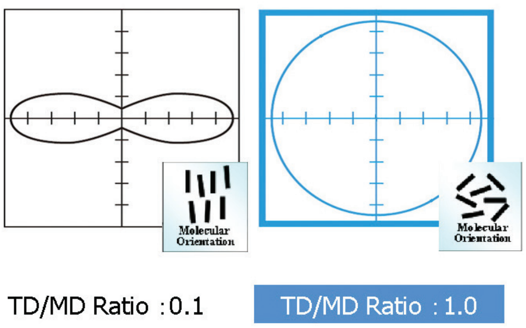
Like SUMIKASUPER E and S Series injection molding grades, thin films made from the new VR Series varnishes offer:

- High temperature stability,
- Excellent thermal conductivity,
- Outstanding dielectric properties — especially low dielectric tangent at high frequencies,
- Exceptional water vapor-barrier properties,
- Good acoustic damping,
- Good surface hardness,
- Excellent dimensional stability,
- Homogeneous in-plane film properties (less anisotropy than molded LCPs),
- Ability to modify via high filler loadings,
- Ability to coat / impregnate sheet-form substrates.

Presently, there are two grades within the VR Series that have been specifically formulated for use on flexible and rigid CCLs and acoustical diaphragms for speakers and headphones. These products share the same base chemistry. However, since they have been formulated with different monomer ratios and so on, there are subtle differences in specific properties such as tensile strength, moisture-absorption rate, and thermal conductivity (see Table III later in this guide). Basic product details are shown in the table below.

Typical properties of thin films produced via solvent casting

Grade Name	Solvent	Typical Use	Solids Content (wt-%)	Viscosity (mPa•s) as measured
VR300 AN8	NMP	Flexible CCLs, headphone diaphragms, & other ductile / moveable substrates	8	300~1,200
VR500 AN24	NMP	Metal-base CCLs & other more rigid substrates	24	400~900



Differences in molecular orientation between extruded (left) and cast (right) LCP films

Supplied in the form of a liquid varnish, SUMIKASUPER VR Series products should be converted to thin films via the solvent casting method using NMP solvent. These films are characterized by homogeneous, in-plane molecular orientation[6]. Because the shear stresses applied during solvent casting are low and limited, the process yields thin films characterized by limited molecular orientation in the micro range and non-orientation in the macro range. On the other hand, LCP films produced via conventional LCPs using the melt-extrusion process are characterized by heterogeneous in-plane film properties owing to molecular orientation caused by the shear stresses induced during the conversion process. This anisotropy has a negative impact on the strength and dielectric properties of thin films and therefore necessitates additional process steps to reduce orientation via stress relaxation to produce usable LCP films — a requirement that adds time and cost. In contrast, the low in-plane anisotropy that characterizes films produced with VR Series LCPs eliminates the need for post-process stress relaxation and are considered major benefits of these new products.

6 The VR series products do produce films with different orientation and coefficient of (linear) thermal expansion (CLT or CLTE) in the through-thickness (Z-) axis vs. the in-plane (X and Y)-axes.

04

Soluble LCPs: Preliminary Application Uses & Benefits

Thin films produced from SUMIKASUPER VR Series products are ideal for use on applications requiring high thermal conductivity, dielectric properties, and vapor-barrier properties.

Copper-Clad Laminates for Printed Circuit Boards

SUMIKASUPER VR300 AN8

SUMIKASUPER VR300 AN8 is the grade specifically formulated for use as a dielectric coating on *flexible* CCLs, which are indispensable components for high-speed power cables connecting flexible (polymer-based) printed circuits (FPCs) to mother boards. As such, they are used in mobile phones, laptops, digital cameras, hand-held games, etc.

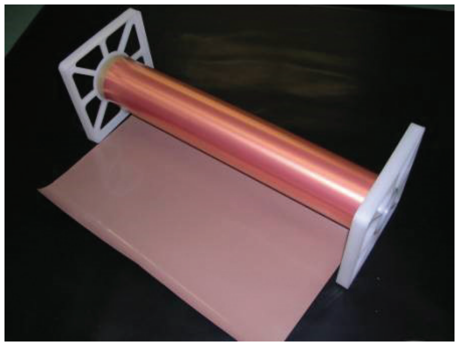
For conventional (flexible) CCLs, the film offers the following properties:

- Outstanding dielectric properties at high frequencies,
- Protection from fluctuating environmental conditions (e.g. temperature, humidity, etc.),
- Low moisture pickup,
- Excellent water-vapor and oxygen barrier properties,
- Excellent temperature resistance below glass-transition temperature[7].

Versus polyimide (PI) in flexible CCLs, thin films produced from the new VR Series offer lower moisture absorption and superior dielectric properties. And, versus thin films produced with conventional LCPs via melt-extrusion, VR Series films offer low in-plane anisotropy and produce more stable films that are far less prone to distortion / warpage.

7 If and when VR Series LCPs are used without fillers to produce thin films, then they should be used below their glass-transition temperature (T_g). If fillers are used — particularly inorganic fillers — then the effects of T_g can be somewhat offset. However, each user should evaluate the appropriate usable temperature range for its own products to determine if VR Series soluble LCP films will be appropriate.

Copper-Clad Laminates for Printed Circuit Boards continued



Solvent-cast LCP films on a polymer base prior to use on flexible CCLs

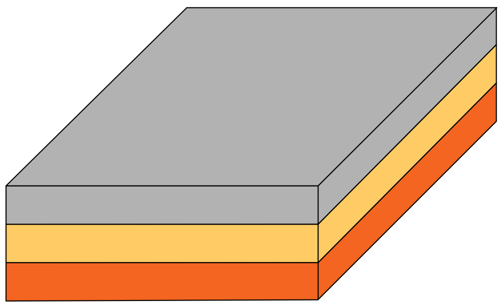
SUMIKASUPER VR500 AN24

SUMIKASUPER VR500 AN24 is the grade specifically formulated for use as a dielectric coating on more rigid metal-based CCLs, which are used in applications where high heat dissipation is important. As such, they are important components for LED lighting, LCD TVs, tablet computers, and in a variety of automotive electronics, including electric power steering, DC/DC converters, air-conditioner inverters, headlights, heads-up displays, and on-board chargers for battery electric vehicles.

Versus competitive ceramic, aluminum, or glass/epoxy fabrics traditionally used in metal-based CCLs, thin films produced from the new VR Series offer excellent thermal conductivity and allow for use of high filler loadings.

For metal-based CCLs, the film offers the following properties:

- Excellent thermal conductivity, and
- Ability to use high-filler loadings to further modify properties.



Solvent-cast films showing use on metal-base CCLs
(grey layer=aluminum; orange layer= soluble LCP; red layer= copper)

When specifying a film material to protect either flexible or rigid (metal-based) CCL, it will be important to match the coefficient of thermal expansion (CTE) properties of the film's base resin as closely as possible with that of either the polymer or copper foil on which it will be coated to avoid warpage and distortion.

A variety of fillers (e.g. silica, alumina, boron nitride, etc.) may be used to modify film properties (e.g. moisture absorption, thermal conductivity, dielectric tangent, coating viscosity, film modulus, etc.) for CCLs. These would be added during the process of dissolving the varnish in NMP solvent. Users should test to determine which, if any, fillers should be used and at what let-down ratio.

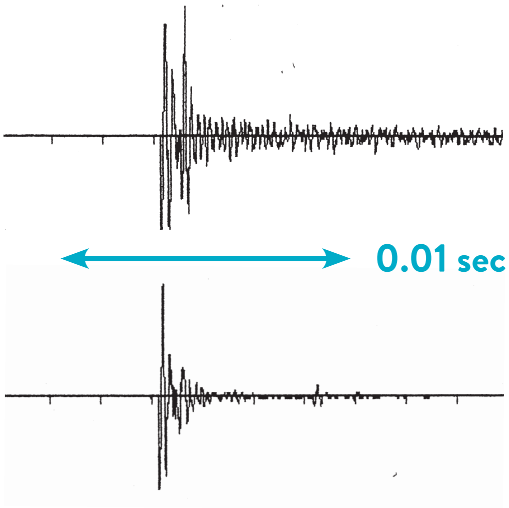
06

Highly Functional Speaker / Headphone Diaphragms

SUMIKASUPER VR300 AN8

SUMIKASUPER VR300 AN8 is the grade specifically formulated for use as the diaphragm membrane used in speakers and headphones. Benefits the VR Series film brings to this application includes:

- Achieve excellent LCP properties in a film that is not oriented,
- Excellent damping properties,
- Ability to modify diaphragm functionality through selection of fillers,
- Easy processability on polyimide-film-producing equipment, and
- Ability to hot-press (mold) 3D parts.



Top image: another engineering polymer coating
Bottom image: SUMIKASUPER soluble LCP film

Versus paper diaphragms, thin film diaphragms produced from the new VR Series offer far lower moisture absorption, so the device's acoustical properties are less likely to change as humidity levels fluctuate and affect sound transmission. And, versus thin films produced with polymers like polyphenylene sulfide (PPS) or polyethylene terephthalate (PET), VR Series films offer superior vibration damping, yielding a clearer sound with less distortion.

07

Soluble LCPs: Processing Information

As noted previously, SUMIKASUPER VR products are supplied in liquid varnish form. To assure high quality, although if stored at room temperature, the stability of the product should not change if consumed within a reasonable period of time. Dispose of contents/container appropriately in accordance with local, regional, national, and international regulations.

The film manufacturing method described in the pages that follow is one approach to using VR varnish. Please adjust method details according to your desired film characteristics.

Step 1: Preparing the Varnish

When stored at room temperature, over time SUMIKASUPER VR varnish may either change viscosity (VR300 AN8) or resin may precipitate out of solution (VR500 AN24). Before proceeding to solvent casting, it is important to re-dissolve precipitated polymer back into the varnish to prevent particles from depositing and causing pinholes in the cast film. Either varnish can be returned to its original state by slowly reheating for 2-6 hours at a temperature of 85-95°C. For small batches, heat the varnish in its original shipping container (cover removed but laid over the container); for bigger batches, multiple shipping containers can be opened and emptied into a large vessel. Slow heating — at a speed no faster than 2°C/minute — is important to avoid a poor appearance later. Do not heat either varnish in a water bath, as water vapor may mix into the varnish.

After heating, the varnish should be cooled to a temperature of 50°C or less before proceeding to the next step. The product should be used within 24 hours after heating to keep polymer from re-precipitating out of the solution. If it does, the product should not be reheated more than 3 times to avoid degradation of the polymer.

If the intention is to add filler to SUMIKASUPER VR varnish, then that should be done before proceeding to the solvent-casting step. If filler is added to the varnish, stir the solution well to assure a homogenous mixture before proceeding to the next step.

Soluble LCPs: Processing Information
Continued

Step 2: Solvent Casting in NMP

For good adhesion of cast film to substrate, the latter should be free of oil, dust, fingerprints, and other contaminants.

During the casting process, SUMIKASUPER VR should be applied as evenly as possible to achieve a good film on the substrate. The product also can be used to impregnate a glass cloth or non-woven fabric. It may be necessary to remove air bubbles to achieve a consistent coating. We recommend that the final cast film thickness not exceed 300 μm as thicker coatings may reduce film-thickness accuracy. We do not set a minimum film thickness as that is dependent on the desired properties of the final film, whether or not filler is used and the average particle size of that filler, the viscosity each customer can handle, etc. Users should test to find the best film thickness that meets the needs of their applications. If the initial film layer is found to be too thin, please let it dry, then re-cast/add another layer of film to increase its thickness. If the initial film is too thick, reduce the coating thickness upon further application.

Soluble LCPs: Processing Information

Continued

Step 3: Drying & Annealing the Film

After coating, the substrate must first be heated to drive off solvent so the material can be handled. The drying step is accomplished using a hot air dryer starting at 40°C and then slowly raising the temperature to 60°C over a period of 2-4 hours. To avoid a poor surface appearance later, researchers suggest that temperature not be raised faster than 0.2°C/minute. After this step, the cast film will appear transparent.

The next step is to anneal the coating to achieve high crystallinity and molecular orientation. Annealing is done at standard conditions of 250-300°C for 3 hours. To prevent deterioration of the film due to oxidation and precipitation of the polymer in the presence of oxygen, the dried film should be annealed in a nitrogen atmosphere where oxygen in the reactor is ≤500 ppm. Annealing is critical to ensure the durability and superior performance of the SUMIKASUPER VR film. After this step, the cast film will turn opaque.

Last, the film and substrate are cooled back down to ≤50°C. At this point in the process, cooling rate is unimportant as it does not affect final film properties.

During the annealing process, users will note that the film's optical properties change. Initially clear and transparent, after annealing, the film will be amber and opaque. Although this change is useful to note, it is not sufficient to use as a quality-control check. Rather, other parameters, such as polymer melting point, are more useful for indicating if molecular weight increases occurred correctly.

The next two tables provide casting and drying conditions for films produced from SUMIKASUPER VR products as well as general properties of initial varnish and final films from these products. Data shown are considered representative but do not constitute any warranty or guarantee.

Casting & Drying Conditions for Films Produced from SUMIKASUPER VR Series Grades

Solvent-Cast Films Made with SUMIKASUPER VR Series Grade		
Grade name	VR300 AN8	VR500 AN24
Substrate	Copper foil	
Casting thickness [μm]	200~250	
Drying condition	40-60°C for 2-4 hours	
Thickness after drying [μm]	8-10	20-25

Soluble LCPs: Processing Information

Continued

General Properties of SUMIKASUPER VR Series Varnishes

Form Factor	Property & Test Condition	Varnish* Made from Grade SUMIKASUPER VR Series VR300 AN8	VR500 AN24	Test Method
Varnish	Solvent	NMP	NMP	—
	Solids content [wt-%]	8	24	—
	Viscosity [mPa•s]	300–1200	400–900	@23°C
Film	Tensile strength [MPa]	145	95	ISO 527-3
	Elongation [%]	24	7	
	Tensile modulus [MPa]	5100	4500	
	Coefficient of linear thermal expansion [x10^{-6}/°C] 2nd (50–100°C)	29	38	50–250°C 5°C/min✦
	1% Loss temperature [°C] in Air	419	394	ISO 7111
	Moisture absorption rate [%]	0.5	0.9	ISO 62
	Glass-transition temperature T_g [°C]	184	210	DMA
	Vapor permeation rate [g/m^2•atm•day] 40°C, 90% RH	0.04 @ 26 µmt	0.07 @ 28 µmt	ISO* 15106
	Dielectric constant (Dk)/ Dielectric tangent (Df) [–] 1GHz	3.4/0.003	3.4/0.004	Impedance analyzer
	Thermal conductivity [W/m•°K]	0.19	0.33	Temperature wave analysis method

* Properties measured on varnishes produced via solvent casting.

✦ As derived from thermomechanical analysis (TMA).

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Feburary 2024