TECHNICAL UPDATE

CRAY VALLEY
A BRAND OF TOTAL

BENEFITS

- Lower viscosity
- Commercially available
- Sustainable feedstock

SUGGESTED MARKETS/ APPLICATIONS

- Specialty adhesives and sealants
- Coatings
- Thermoplastic Urethanes
- Encapsulants for electronics

ADDITIONAL INFO

- **SDS/TDS:** Krasol® LBH-P 3000, Krasol F 3000
- **Press Release:** TOTAL Cray Valley introduces Krasol F 3000, the first PolyFarnesene Diol
- T. Yoo and S. Henning, *Rubber Chem Technol.*, 90(2), 308 (2017)

Krasol® F 3000 Novel Bio-Based Diol for Polyurethanes

Introduction

Krasol® polybutadiene diols have long been used to prepare polyurethanes with low temperature flexibility and excellent hydrolytic stability. TOTAL Cray Valley is pleased to announce the addition of a new member to the Krasol family: Krasol F 3000, based on **sustainable**, non-petroleum derived feedstocks.

Krasol F 3000, a polyfarnesene diol, is produced from *trans*-β-farnesene, a bio-based monomer produced by Amyris under the tradename Biofene®. Amyris produces Biofene from sustainable feedstocks at high purity in commercial quantities. As with Krasol polybutadiene diols, TOTAL Cray Valley produces Krasol F 3000 via anionic polymerization, providing well-defined microstructure, narrow molecular weight range, and near quantitative terminal hydroxyl functionality (2.0). In addition, the unique structure of polyfarnesene allows Krasol F 3000 to have a **reduced viscosity at equivalent molecular weight**, enabling more freedom in polyurethane processing and formulation.

Krasol F 3000 Properties

Both Krasol LBH-P 3000 and Krasol F 3000 are primary hydroxyl terminated diols of similar molecular weight. Due to the unique "bottle brush" structure of polyfarnesene diol, Krasol F 3000 has much lower viscosity, while still having narrowly defined hydroxyl functionality and vinyl content. Figure 1 shows the structure of Krasol F 3000, while Table 1 shows its typical properties compared to Krasol LBH-P 3000. The viscosity of Krasol F 3000 is comparable to commercially available polyether diol of higher molecular weight, as shown in Figure 2.

TOTAL
COMMITTED TO BETTER ENERGY

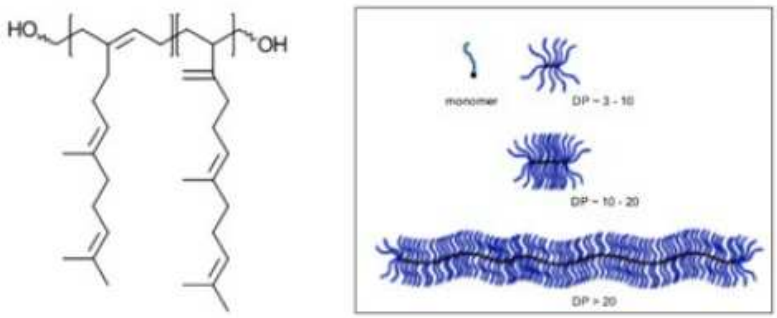

Figure 1: Structure of Krasol F 3000.

Table 1: Typical properties of Krasol LBH-P 3000 and Krasol F 3000.

Property	Krasol LBH-P 3000	Krasol F 3000
Viscosity at 25 °C, cP	**13,000**	**1,700**
Average molecular weight Mn, g/mol	**3,000**	**3,000**
Polydispersity index, Mw/Mn	1.1-1.3	1.1-1.3
Terminal OH groups	Primary	Primary
OH equivalent, meq/g	0.6-0.7	0.6-0.7
Glass transition temperature, °C	-44	-65
Specific gravity at 20 °C, g/cm³	0.89	0.90
APHA color	20	20
Microstructure, wt% 1,2-vinyl	65	-
3,4-vinyl	-	40
1,4-cis + 1,4-trans	35	60

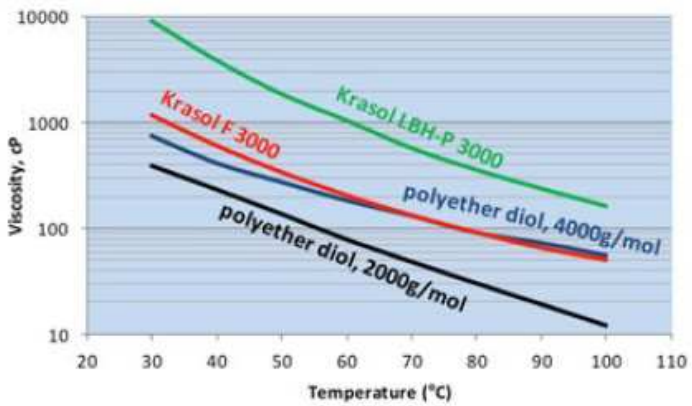

Figure 2: Viscosity vs. Temperature of Krasol LBH-P 3000, Krasol F 3000, and commercially available polyether diols.

Performance of Krasol F 3000 in Polyurethane Formulations

Krasol LBH-P 3000, Krasol F 3000, and a 50-50 blend of the two were prepared in a model 40% hard segment polyurethane formulation as shown in Table 2. These polyurethanes were prepared via a two-step process. First the prepolymer was prepared from the polyol(s) and the isocyanate, followed by the addition of chain extender and catalyst. These mixtures were cured at 85 °C, then evaluated. Table 3 shows a summary of the results.

Table 2: Polyurethane Formulation.

Ingredient	Purpose	Parts per 100 parts Krasol
Krasol LBH-P 3000, Krasol F 3000, or 50/50 mix	Polyol	100
Mix of 2,4' and 4,4'-Diphenylmethane Diisocyanate	Isocyanate	45.2
2-Ethyl-1,3-Hexanediol	Chain Extender	21.4

**Catalyzed with three drops of 20% dibutyltin dilaurate in dibutyl phthalate*

Table 3: Cured Polyurethane Evaluation Results.

Ingredient	Purpose	Krasol LBH-P 3000	50:50 Krasol Mix	Krasol F 3000
Process viscosities at 25 °C, cP	Krasols	12,888	4,424	1,687
	Polyol Premix	5,741	2,296	947
	Prepolymer	11,787	4,340	1,687
	Formulation Without Catalyst	1,443	730	360
Hardness, shore A [1]		85	82	80
Dielectric strength, V/mil (KV/mm) [2]		516 (20.3)	-	555 (21.8)
Dissipation factor [3]		0.01754	-	0.01154
Dielectric constant [3]		2.592	-	2.633
Glass transition temperature, °C [4]		-38	-46	-59
Water vapor transmission rate, g/(hxm²) [5]		0.0173	-	0.0122
Permeance, ng/(Paxsxm²) [5]		3.83	-	2.69

(1) ASTM D2240 Shore A; (2) ASTM D149 Short time test method A; (3) ASTM D150 @ 1000 Hz; (4) via DSC; (5) ASTM E96 at 23 °C and 50% relative humidity via water method. Note permeability is permeance x thickness of specimen being measured.

Krasol F 3000 has a significantly lower viscosity compared to Krasol LBH-P 3000, thus the viscosities during preparation are lower as well. This can provide more freedom in polyurethane formulation development, as well as enable spray applications requiring low viscosity.

Krasol F 3000 would be beneficial in an electric insulation or encapsulant application, given its slightly higher dielectric breakdown strength and lower dissipation factor. In architectural sealant applications, Krasol F 3000 would be advantageous given its lower water vapor transmission rate and permeability, and its lower Tg would provide better low temperature performance. A range of these properties could be obtained by blending the Krasols in the formulation. Substitution or addition of other diols could further lower viscosity, and altering the isocyanate to polyol ratio could improve mechanical properties.

Summary

Krasol polybutadiene diols are used in polyurethane formulations to impart improved moisture resistance, low temperature flexibility, and greater impact resistance. The new Krasol polyfarnesene diol, Krasol F 3000, can provide comparable properties, but also has the benefit of lower viscosity. Tg is lower as well for improved low temperature performance. It may also improve electric insulative properties and water resistance. Krasol F 3000 is sustainably sourced from bio-based feedstock in commercial quantities and is a viable alternative to polyester and polyether diols in polyurethane formulations.

Regulatory Compliance

No license is required by the US Department of Commerce for Krasol F 3000 export. Krasol F 3000 is listed on the US TSCA inventory. Krasol F 3000 is a polymer and thus is exempt from registration with REACH.

About TOTAL Cray Valley

TOTAL Cray Valley is the premier global supplier of specialty chemical additives, hydrocarbon specialty chemical, and liquid and powder tackifying resins used as ingredients in adhesives, rubbers, polymers, coatings and other materials. TOTAL Cray Valley has pioneered the development of these advanced technologies, introducing hundreds of products that enhance the performance of products in energy, printing, packaging, construction, tire manufacture, electronics, and other demanding applications.

For more information, please visit **www.crayvalley.com**

TOTAL Cray Valley (TCV)
665 Stockton Drive, Suite 100
Exton, PA 19341, USA
1.877.US1-CRAY

*The listed properties are illustrative only, and not product specifications. TOTAL Cray Valley disclaims any liability in connection with the use of the information, and does not warrant against infringement by reason of the use of its products in combination with other materials or in any process.

CV1286.08.17