ANACARDA TECHNICAL ARTICLE

FAST THIN FILM CURE ALLOWING A SPEEDY RETURN TO SERVICE

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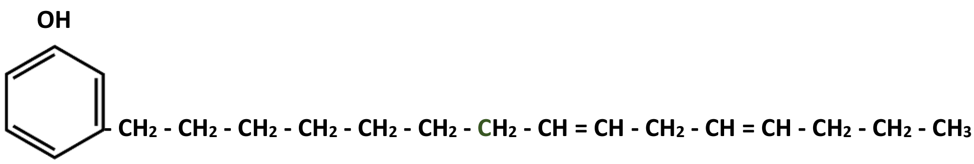
Introduction

Anacarda Ltd is named after the tropical tree that bears the fruit of its primary raw material feedstock, Anacardium occidentale or the Cashew Nut tree. Anacarda specialises in Cashew Nutshell liquid [CNSL] derivatives and the generation of niche polymers that convey desirable characteristics because of the unique chemical structure of this interesting biomass.

Background

CNSL is recognised as being one of the most abundant commercialised renewable feedstocks for a variety of applications. [1] It is a dark liquid that is extracted from within the protective shell of the Cashew Nut. Being inedible it is not disruptive to the food chain. The crude CNSL may be used in some phenolic polymer applications but for epoxy-based curing agents it is usually refined to generate Cardanol. Cardanol has a substituted phenol structure as depicted below.

Figure 1. Fundamental Cardanol structure

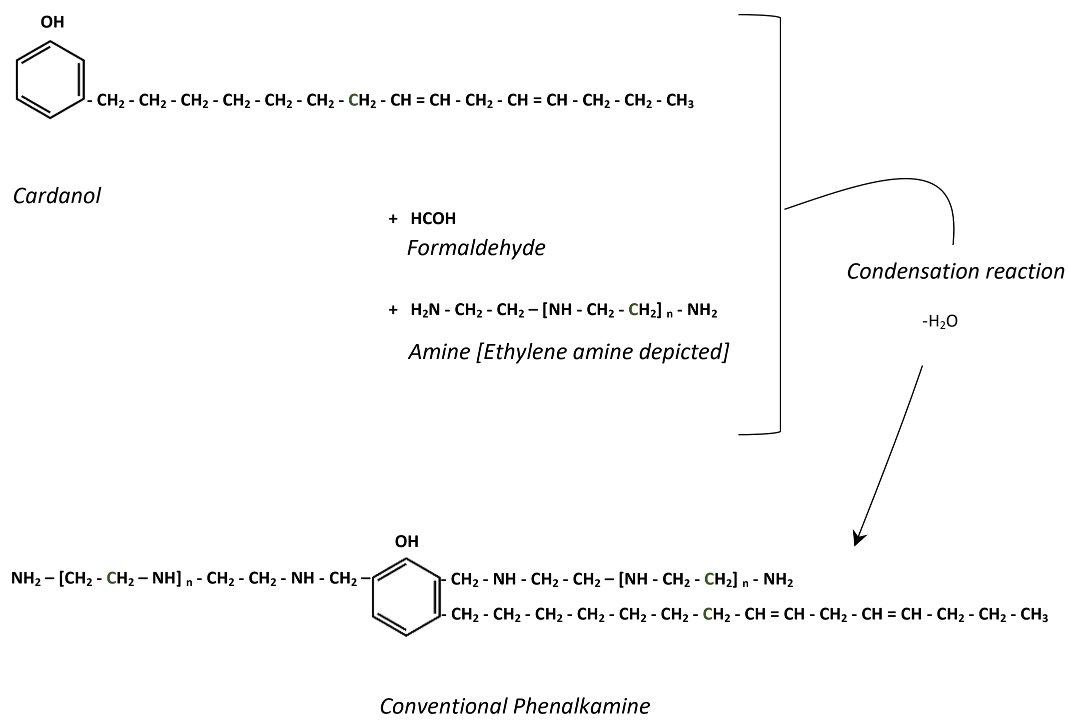


Cashew Nuts are harvested in several tropical locations. India, and to a lesser extent Vietnam, have the largest throughput of the extracted oil and the subsequent refinement process that generates the Cardanol component. As may be expected, India is also the largest producer of the conventional Phenalkamines.

Reaction of the Cardanol with formaldehyde and an amine yields the Mannich base referred to as a "Phenalkamine". This term was coined by 3M in the 1970's. [2]

The reaction process is depicted below.

Figure 2. Generic Phenalkamine process



Phenalkamines come in numerous guises but have the general structure detailed above. There are of course several variances as a result of the selected amine[s], mole ratio of components, and the process conditions. Subsequent modifications are made through optional adduction with epoxy resins[s], accelerator addition, and/or solvation. Typical solvents are Xylene or combinations of Xylene and n-Butanol employed in sufficient quantity to reduce the viscosity to a manageable level. All of these factors and the subsequent modifications will have an effect and impact on the stoichiometry and subsequent use.

The Phenalkamine structure conveys an inherent hydrophobicity because of the long alkyl side chain attached to the Phenolic nucleus. This in turn contributes to greater flexibility and the excellent corrosion protection that is associated with this generic class of curing agent. Mannich bases are notoriously fast curing and suitable for cure under adverse conditions with Phenalkamines being no exception. The conventional Phenalkamines have been available for many years and there are many manufacturers offering these product types. Although perfectly capable of processing conventional Phenalkamines, Anacarda tend to focus on speciality products that offer enhanced technical performance and/or regulatory compliance. Building on the benefits attributed to Phenalkamines and the advantages afforded by their unique structure, we have innovatively progressed the chemistry of these materials to bring a new generation of Phenalkamines to market offering significant advantages over existing materials.

The latest generation of Phenalkamine curing agents offer many of the attributes that the existing technology is renowned for and maintain the excellent corrosion protection, flexibility, and substrate wetting. They do however convey some additional improvements. All of the new grades are compliant with the REACH [Registration, Evaluation, Authorisation and Restriction of Chemicals] regulations and in many cases provide lower residual free monomer levels than the conventional grades.

To demonstrate some of the performance properties and benefits offered by the new series we have selected CARDAMINE H811.

Property profile

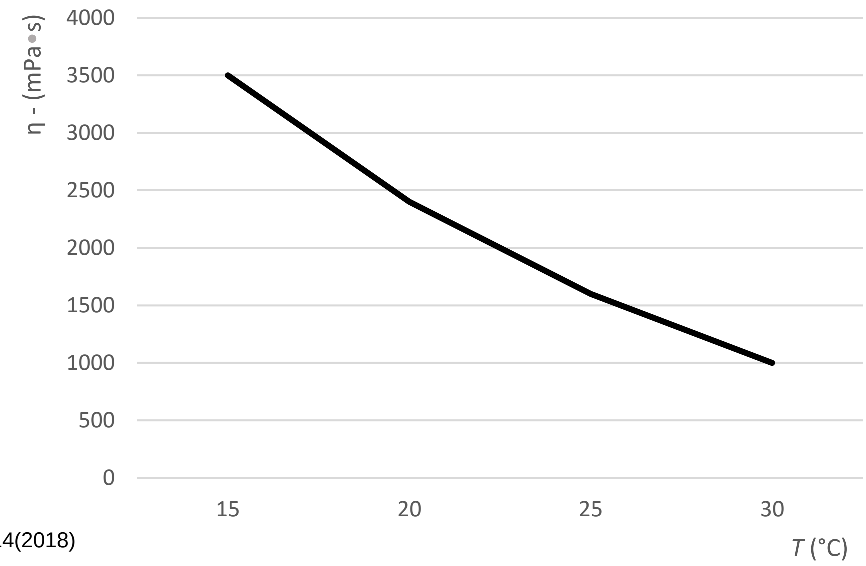
CARDAMINE H 811 is a low viscosity, high reactivity grade that has some excellent features. It is free from solvent or diluent and provides rapid thin film cure and property development even at low temperatures.

Table 1 Physical Properties

Physical Property	Units	Method	Minimum	Maximum
• Colour	Gardner	ASTM D1544-04(2018)	-	18
• Viscosity @ 25°C	mPa•s	ASTM D2556-14(2018)	500	4500
• Gel-time reactivity [100:70] *	Minutes	ASTM D3056-14(2018)	30	60
Density @ 25°C	g/cm^3	ASTM D891-18	0.95	1.05

* Gel-time reactivity is undertaken as a combined 150 Gm mass with EPILOK 60-600 [Bitrez Ltd] liquid epoxy resin with EEW ≈ 190. The independent materials are equilibrated at 25°C before being combined in the designated ratio. This semi-adiabatic test is undertaken with a Techne gel-timer to determine the end point.

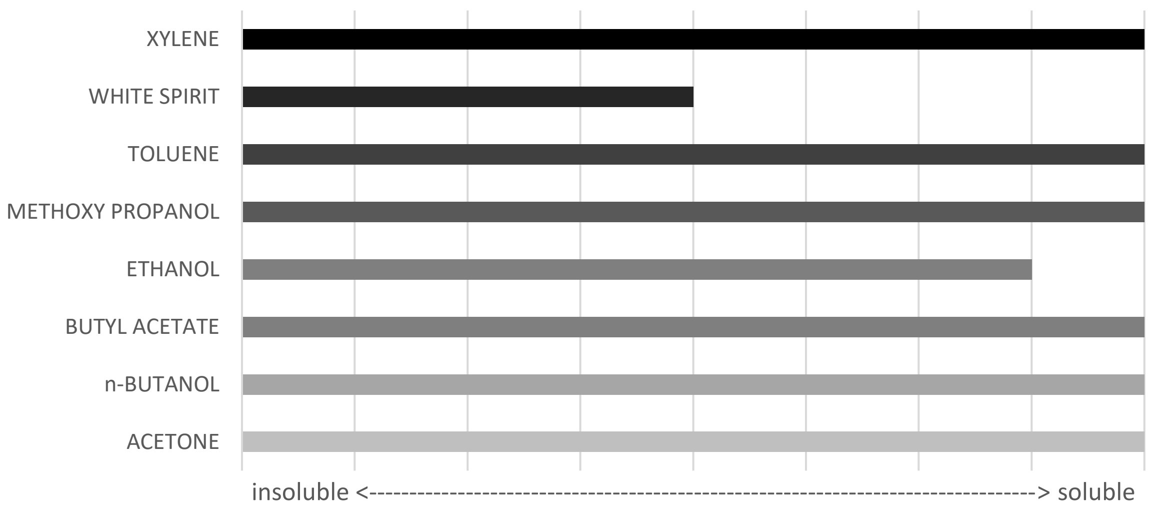
Figure 3 viscosity vs temperature



ASTM D2556-14(2018)

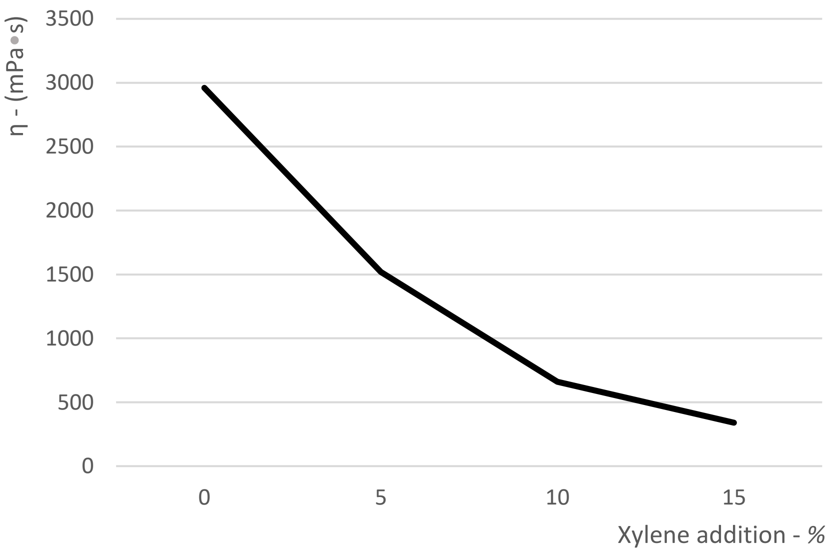
CARDAMINE H 811 is inherently low in viscosity but should it require dilution with solvent to further reduce viscosity it exhibits excellent solubility in a broad range of solvents including.

Figure 4 Solvent solubility chart



This grade is soluble in a wide variety of solvents although Xylene is more typically used for diluting systems formulated with Phenalkamines. This grade is inherently low in viscosity as stated but should it be diluted with Xylene it cuts very quickly.

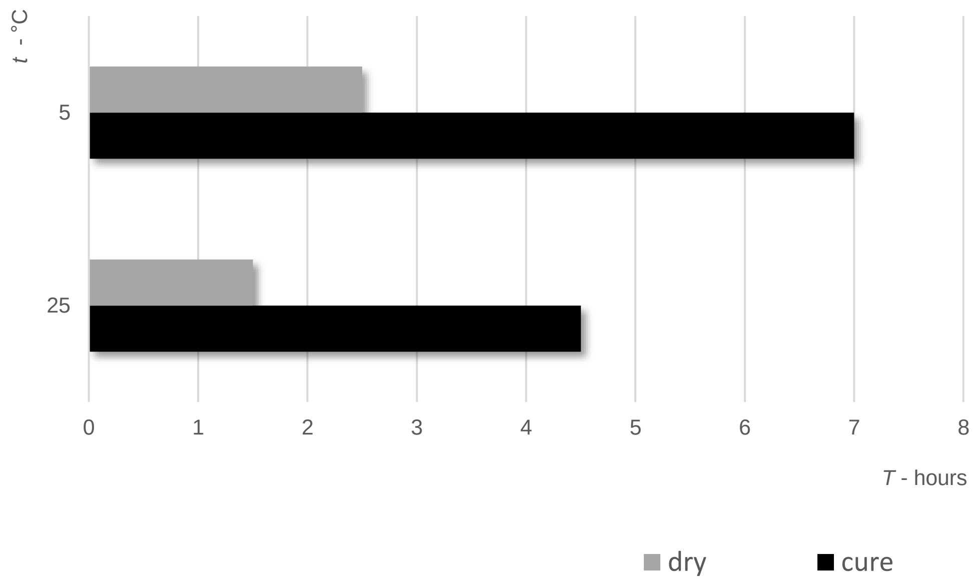
Figure 5 viscosity vs xylene addition



The latest series of CARDAMINE grades exhibit even further improvement to cure response at low temperatures without a significant reduction in pot-life. CARDAMINE H811 offers excellent reactivity and cure response. Several cure schedules may be employed including ambient curing although if solvated systems are employed then the cure rates will be influenced by the chosen solvent system.

CARDAMINE H811 will cure at low temperatures [0°C] and under adverse conditions. The rate of cure may be accelerated through both the application of heat and/or inclusion of accelerators.

Figure 6 Dry times and cure times



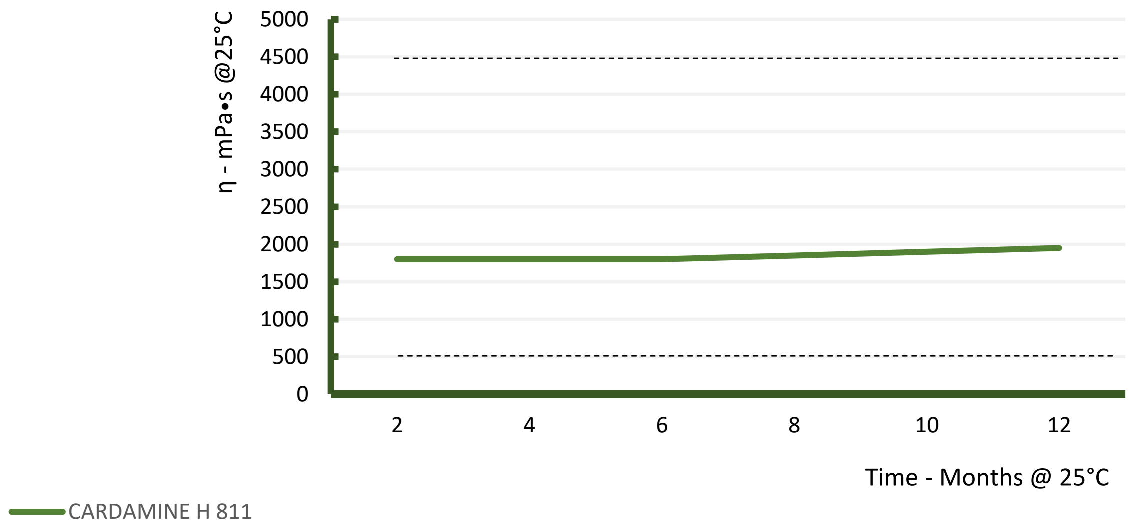
The graph above depicts the thin film reactivity at the temperatures indicated in the chart. Evaluation has been undertaken in combination with a stoichiometric quantity of EPILOK 60-600 [Bitrez Ltd], a liquid epoxy resin with EEW ≈ 190.

Cured films are clear, smooth, and glossy at both 25°C and 5°C.

Product stability

Mannich base curing agents can increase in viscosity over time and whilst these products are generally considered stable, they can chemically alter on storage, especially if subjected to higher ambient temperatures. Prolonged elevated temperature storage can induce molecular weight build and associated changes in viscosity. Occasionally, amine can be liberated, especially if the more volatile amine species have been employed. The new grades offer excellent storage stability as indicated in the figure below. [Viscosity upper limit 4500 mPa•s]

Figure 7 Stability evaluation



Viscosity conducted with a Brookfield viscometer @ 25C [ASTM D2556-14] and the material stored in sealed containers @ 25°C. In the case of the reactivity following storage, there was no appreciable difference.

Bio-based Carbon content [3]

Biobased Carbon % indicates the percentage carbon from “natural” (plant or animal by-product) sources versus “synthetic” (petrochemical) source. For reference, 100 % Biobased Carbon indicates that a material is entirely sourced from plants or animal by-products and 0 % Biobased Carbon indicates that a material did not contain any carbon from plants or animal by-products. A value in between represents a mixture of natural and fossil sources. The analytical measurement is cited as “percent modern carbon (pMC)”. This is the percentage of C14 measured in the sample relative to a modern reference standard (NIST 4990C). The % Biobased Carbon content is calculated from pMC by applying a small adjustment factor for C14 in carbon dioxide in air today. It is important to note is that all internationally recognized standards using C14 assume that the plant or biomass feedstocks were obtained from natural environments. Reported results are accredited to ISO/IEC 17025:2005 Testing Accreditation PJLA #59423. The result is relative to total carbon (TC) or total organic carbon (TOC).

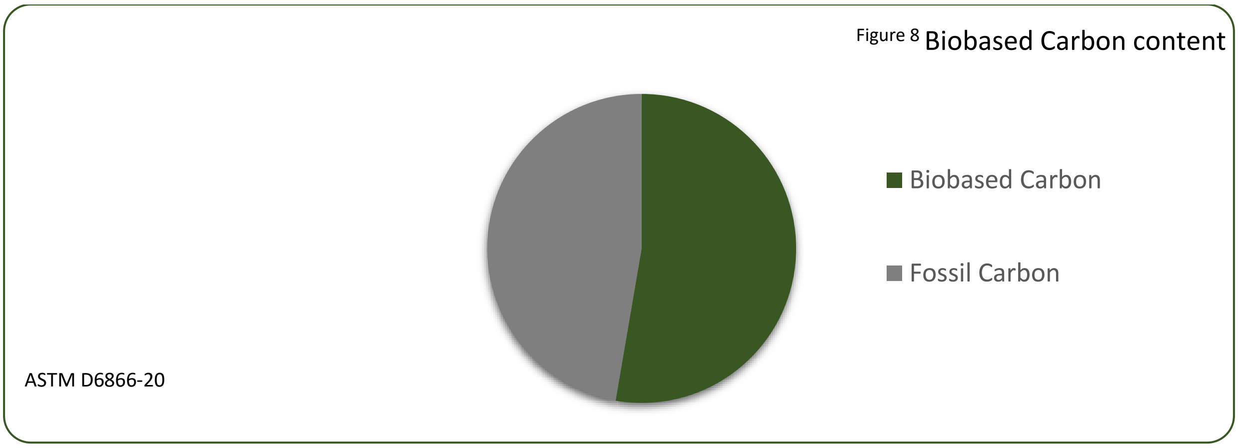


Figure 8 Biobased Carbon content

% Biobased Carbon Content	
Result	52.7%

Summary

The new series of CARDAMINE epoxy curing agents are derived from sustainable feedstock and offer outstanding speed of cure. They are available in several forms including supply as low viscosity solvent free liquids and with high solids content. They are compliant with REACH and other regulatory requirements.

These products offer excellent reactivity profiles and they cure under difficult, adverse conditions. They are hydrophobic and provide excellent corrosion protection. The latest generation of CARDAMINE grades are the Phenalkamine of choice for the Marine and Protective Coatings market.

References

1. Author: Sylvain Caillol Publication: Current Opinion in Green and Sustainable Chemistry Publisher: Elsevier Date: December 2018
2. Cardolite website www.cardolite.com
3. Beta analytical testing Laboratory – test report 2020