

## Cashew Nutshell Liquid Resin

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**Abstract**— CNSL (The cashew nutshell liquid) or cashew shell oil is a natural resin found in the honeycomb structure of the cashew nutshell and is a byproduct of processing cashew nuts. Its composition varies depending on how it is processed. Cold, solvent extracted CNSL is mostly composed of anacardic acids (70%), cardol (18%) and cardanol (5%) These substances are dermatogenic, like the oils of the poison ivy, and present danger during manual cashew processing.

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### 1. INTRODUCTION

The cashew nutshell liquid (CNSL) or cashew shell oil is a natural resin found in the honeycomb structure of the cashew nutshell and is a byproduct of processing cashew nuts. Its composition varies depending on how it is processed. Cold, solvent extracted CNSL is mostly composed of anacardic acids (70%), cardol (18%) and cardanol (5%) These substances are dermatogenic, like the oils of the poison ivy, and present danger during manual cashew processing.

It is a raw material of multiple uses in developing drugs, antioxidants, fungicides, etc. It is used in tropical folk medicine and for anti-termite treatment of timber.

The anacardic acids have been used effectively in vivo against tooth abscesses due to their lethality to a wide range of gram-positive bacteria. Many parts of the plant are used by the Patamona of Guyana medicinally. The bark is scraped and soaked overnight or boiled as an antidiarrheal. Seeds are ground up into powders used for antivenom for snake bites. The nut oil is used topically as an antifungal and for healing

cracked heels.

Heating CNSL decarboxylates the anacardic acids, producing a technical grade of CNSL that is rich in cardanol. Distillation of this material gives distilled, technical CNSL containing 78% cardanol and 8% cardol (cardol has one more hydroxyl group than cardanol) This process also reduces the degree of thermal polymerization of the un-saturated alkyl-phenols present in cashew shell nut liquid. This natural oil phenol has been found to have interesting chemical structural features which enable a range of chemical modifications to create a wide spectrum of bio-based monomers capitalising on the chemically versatile construct it containing three different functional groups, the aromatic ring, the hydroxyl group and the double bonds in the flanking alkyl chain.

These can be split into key groups, there use as Polyols. Which have recently seen a dramatic increase in demand for their bio-based origin and key chemical attributes such as high reactivity, range of functionalities, reduction in blowing agents and naturally occurring fire retardant properties in the field of ridged polyurethanes aided by their inherent phenolic structure and larger number of reactive units per unit mass. CNSL based Novolac are another versatile industrial monomer deriving from cardanol typically used as reticulating agents for epoxy matrices in composite applications providing good thermal and mechanical properties to the final composite material. Further examples of applications which are Cashew shell nut liquid derived materials are being evaluated are in the fields of chemical intermediates, additives, stabilizers, lubricants, diesel engine fuel alternatives, pour point dispersants, anti-oxidants, anticorrosive paints. Abrasives and friction dusts have also been developed from Residol, the residue byproduct of this synthesis process.

During World War II it was used as a sabotage device by SOE (Special Operations Executive) for destroying the engines of German vehicles when poured into the crankcase of engines.

## 2. ASPHALT

Asphalt also known as bitumen, is a sticky, black and highly viscous liquid or semi-solid form of petroleum. It may be found in natural deposits or may be a refined product; it is a substance classed as a pitch. Until the 20th century, the term asphaltum was also used.

"Bitumen", naturally occurring bituminous sands used for petroleum production. The terms bitumen and asphalt are mostly interchangeable, except where asphalt is used as an abbreviation for asphalt concrete.



**Figure.1: Asphalt, Natural asphalt/bitumen from the Dead Sea Refined asphalt/bitumen**

The primary use of asphalt/bitumen is in road construction, where it is used as the glue or binder mixed with aggregate particles to create asphalt concrete. Its other main uses are for bituminous waterproofing products, including production of roofing felt and for sealing flat roofs.

The terms *asphalt* and *bitumen* are often used interchangeably to mean both natural and manufactured forms of the substance. In American English, asphalt (or asphalt cement) is the carefully refined residue from the distillation process of selected crude oils. Outside the United States, the product is often called bitumen. Geological terminology often prefers the term bitumen. Common usage often refers to various forms of

asphalt/bitumen as "tar", such as at the La Brea Tar Pits. Another term, mostly archaic, refers to asphalt/bitumen as "pitch". The pitch used in this mixture is sometimes found in natural deposits but usually made by the distillation of crude oil.



**Figure.2: Pitch, usually made by the distillation of crude oil**

Naturally occurring asphalt/bitumen is sometimes specified by the term "crude bitumen"; its viscosity is similar to that of cold molasses whilst the material obtained from the fractional distillation of crude oil [boiling at 525 °C (977 °F)] is sometimes referred to as "refined bitumen".

## 3. ETYMOLOGY

The word *asphalt* is derived from the late Middle English, in turn from French *asphalte*, based on Late Latin *asphalton*, *asphaltum*, which is the latinisation of the Greek *ásphaltos*, *ásphalton* a word meaning "asphalt/bitumen/pitch", which perhaps derives from  $\alpha$ - "without" and *sfallō*, "make fall". Note that in French, the term *asphalte* is used for naturally occurring bitumen-soaked limestone deposits, and for specialised manufactured products with fewer voids or greater bitumen content than the "asphaltic concrete" used to pave roads. Another description has it that the term derives from the Accadian term *asphaltu* or *sphallo*, meaning "to split". It was later adopted from the Homeric Greeks as a verb meaning "to make firm or stable", "to secure". It is a significant fact that the first use of asphalt by the ancients was in the nature of cement for securing or joining together various objects, and it thus seems likely that the name itself was expressive of this application.

The expression "bitumen" originated in the Sanskrit, where we find the words *jatu*, meaning "pitch," and *jatu-krit*, meaning "pitch creating", "pitch producing"



(referring to coniferous or resinous trees). The Latin equivalent is claimed by some to be originally *gwitumen* (pertaining to pitch), and by others, *pixtumens* (exuding or bubbling pitch), which was subsequently shortened to *bitumen*, thence passing via French into English. From the same root is derived the Anglo Saxon word *cwidu* (mastix), the German word *Kitt* (cement or mastic) and the old Norse word *kvada*. Neither of the terms asphalt or bitumen should be confused with tar or coal tars.

#### 4. MODERN USAGE

In British English, the word 'asphalt' is used to refer to a mixture of mineral aggregate and asphalt/bitumen (also called tarmac in common parlance). The earlier word 'asphaltum' is now archaic and not commonly used. In American English, 'asphalt' is equivalent to the British 'bitumen'. However, 'asphalt' is also commonly used as a shortened form of 'asphalt concrete' (therefore equivalent to the British 'asphalt' or 'tarmac'). In Australian English, bitumen is often used as the generic term for road surfaces. In Canadian English, the word bitumen is used to refer to the vast Canadian deposits of extremely heavy crude oil,<sup>[7]</sup> while asphalt is used for the oil refinery product used to pave roads and manufacture roof shingles and various waterproofing products. Diluted bitumen (diluted with naphtha to make it flow in pipelines) is known as dilbit in the Canadian petroleum industry, while bitumen "upgraded" to synthetic crude oil is known as syncrude and syncrude blended with bitumen as synbit.

Bitumen is still the preferred geological term for naturally occurring deposits of the solid or semi-solid form of petroleum. Bituminous rock is a form of sandstone impregnated with bitumen. The oil sands of Alberta, Canada are a similar material.

The substance is completely soluble in carbon disulfide, and composed primarily of a mixture of highly condensed polycyclic aromatic hydrocarbons; it is most commonly modelled as a colloid, with asphaltenes as the dispersed phase and maltenes as the continuous phase.

#### 5. ORGANIZED STRUCTURE

One writer stated although a "considerable amount of work has been done on the composition of asphalt, it is exceedingly difficult to separate individual hydrocarbon in pure form" ,and "it is almost

impossible to separate and identify all the different molecules of asphalt, because the number of molecules with different chemical structure is extremely large".

Most natural bitumens contain sulfur and several heavy metals, such as nickel, vanadium, lead, chromium, mercury, arsenic, selenium, and other toxic elements. Bitumens can provide good preservation of plants and animal fossils.

Asphalt/bitumen can sometimes be confused with "tar", which is a similar black, thermoplastic material produced by the destructive distillation of coal. During the early and mid-20th century when town gas was produced, tar was a readily available product and extensively used as the binder for road aggregates. The addition of tar to macadam roads led to the word tarmac, which is now used in common parlance to refer to road-making materials. However, when natural gas succeeded town gas, asphalt/bitumen has completely overtaken the use of tar in these applications. Other examples of this confusion include the La Brea Tar Pits and the Canadian tar sands. Pitch is another term mistakenly used at times to refer to asphalt/bitumen, as in Pitch Lake.

Natural deposits of asphalt/bitumen include lakes such as the Pitch Lake in Trinidad and Tobago and Lake Bermudez in Venezuela), Gilsonite, the Dead Sea, asphalt/bitumen-impregnated sandstones known as bituminous rock and the similar "tar sands". Asphalt/bitumen was mined at Ritchie Mines in Macfarlan in Ritchie County, West Virginia in the United States from 1852 to 1873. Bituminous rock was mined at many locations in the United States for use as a paving material, primarily.

Asphalt/bitumen can be separated from the other components in crude oil (such as naphtha, gasoline and diesel) by the process of fractional distillation, usually under vacuum conditions. A better separation can be achieved by further processing of the heavier fractions of the crude oil in a de-asphalting unit, which uses either propane or butane in a supercritical phase to dissolve the lighter molecules which are then separated. Further processing is possible by "blowing" the product: namely reacting it with oxygen. This makes the product harder and more viscous.

Asphalt/bitumen is typically stored and transported at temperatures around 150°C (300°F). Sometimes diesel oil or kerosene are mixed in before shipping to

retain liquidity; upon delivery, these lighter materials are separated out of the mixture. This mixture is often called "bitumen feedstock", or BFS. Some dump trucks route the hot engine exhaust through pipes in the dump body to keep the material warm. The backs of tippers carrying asphalt/bitumen, as well as some handling equipment, are also commonly sprayed with a releasing agent before filling to aid release. Diesel oil is no longer used as a release agent due to environmental concerns.

## 6. GEOLOGICAL ORIGIN



**Figure.3: Bituminous outcrop of the Puy de la Poix, Clermont-Ferrand, France**

Naturally occurring deposits of asphalt/bitumen are formed from the remains of ancient, microscopic algae (diatoms) and other once-living things. These remains were deposited in the mud on the bottom of the ocean or lake where the organisms lived. Under the heat (above 50 °C) and pressure of burial deep in the earth, the remains were transformed into materials such as asphalt/bitumen, kerogen, or petroleum. Deposits at the La Brea Tar Pits are an example.

There are structural similarities between asphalt/bitumen and the organic matter in carbonaceous meteorites. However, detailed studies have shown these materials to be distinct. The use of asphalt/bitumen for waterproofing and as an adhesive dates at least to the fifth millennium B.C. in the early Indus community of Mehrgarh, where it was used to line the baskets in which they gathered crops.

In the ancient Middle East, the Sumerians used natural asphalt/bitumen deposits for mortar between bricks and stones, to cement parts of carvings, such

as eyes, into place, for ship caulking, and for waterproofing. In some versions of the Book of Genesis in the Bible, the name of the substance used to bind the bricks of the Tower of Babel is translated as bitumen. A one-kilometre tunnel beneath the river Euphrates at Babylon in the time of Queen Semiramis (800 B.C.) was reportedly constructed of burnt bricks covered with asphalt/bitumen as a waterproofing agent. This must be regarded as legendary, but indicative that the concept was known. The Persian word for asphalt is *moom*, which is related to the English word mummy.

In the ancient Far East, natural asphalt/bitumen was slowly boiled to get rid of the higher fractions, leaving a material of higher molecular weight which is thermoplastic and when layered on objects, became quite hard upon cooling. This was used to cover objects that needed waterproofing, such as scabbards and other items. Statuettes of household deities were also cast with this type of material in Japan, and probably also in China. In North America, archaeological recovery has indicated asphalt/bitumen was sometimes used to adhere stone projectile points to wooden shafts.

### 6.1 Early use in Europe

The Greek fire, which composition was a military secret of the Byzantine navy, contained, among other things, asphalt/bitumen as a component. 100 years after the fall of Constantinople in 1453, Pierre Belon described in his work *Observations* in 1553 that *pissasphalto* a mixture of pitch and bitumen was used in Dubrovnik for tarring of ships from where it was exported to a market place in Venice where it could be bought by anyone. An 1838 edition of *Mechanics Magazine* cites an early use of asphalt in France. A pamphlet dated 1621, by "a certain Monsieur d'Eyrinys, states that he had discovered the existence (of asphaltum) in large quantities in the vicinity of Neufchatel", and that he proposed to use it in a variety of ways - "principally in the construction of air-proof granaries, and in protecting, by means of the arches, the water-courses in the city of Paris from the intrusion of dirt and filth", which at that time made the water unusable. "He expatiates also on the excellence of this material for forming level and durable terraces" in palaces, "the notion of forming such terraces in the streets not one likely to cross the brain of a Parisian of that generation". But it was generally neglected in France until the revolution of 1830. Then, in the 1830s, there was a surge of interest, and asphalt became widely used "for pavements, flat roofs, and the lining of cisterns, and



in England, some use of it had been made of it for similar purposes". One of the earliest uses in France was the laying of about 24,000 square yards of Seyssel asphalt at the Place de la Concorde in 1835

Among the earlier uses of asphalt/bitumen in the United Kingdom was for etching. William Salmon's *Polygraphice* (1673) provides a recipe for varnish used in etching, consisting of three ounces of virgin wax, two ounces of mastic, and one ounce of asphaltum. By the fifth edition in 1685, he had included more asphaltum recipes from other sources

The first British patent for the use of asphalt/bitumen was Cassell's patent asphalt or bitumen' in 1834. Then on 25 November 1837, Richard Tappin Claridge patented the use of Seyssel asphalt, for use in asphalt pavement having seen it employed in France and Belgium when visiting with Frederick Walter Simms, who worked with him on the introduction of asphalt to Britain. Dr T. Lamb Phipson claims that his father, Samuel Ryland Phipson, a friend of Claridge, was also "instrumental in introducing the asphalt pavement (in 1836)". Indeed, mastic pavements had been previously employed at Vauxhall by a competitor of Claridge, but without success.

### 6.2 Modern Use: Asphalt Concrete

The largest use of asphalt/bitumen is for making asphalt concrete for road surfaces and accounts for approximately 85% of the asphalt consumed in the United States. Asphalt concrete pavement material is commonly composed of 5% asphalt/bitumen cement and 95% aggregates (stone, sand, and gravel). Due to its highly viscous nature, asphalt/bitumen cement must be heated so it can be mixed with the aggregates at the asphalt mixing plant. There are about 4,000 asphalt concrete mixing plants in the U.S., and a similar number in Europe.

Asphalt concrete road surface is the most widely recycled material in the U.S., both by gross tonnage and by percentage. According to an industry survey conducted by the Federal Highway Administration and the National Asphalt Pavement Association and released in 2011, more than 99% of the asphalt removed each year from road surfaces during widening and resurfacing projects is reused as part of new pavements, roadbeds, shoulders and embankments.

Roofing shingles account for most of the remaining asphalt/bitumen consumption. Other uses include cattle sprays, fence-post treatments, and waterproofing for fabrics.

Asphalt concrete paving is widely used in airports around the world. Due to the sturdiness and ability to be repaired quickly, it is widely used for runways dedicated to aircraft landing and taking off.

### 6.3 Mastic Asphalt

Mastic asphalt is a type of asphalt which differs from dense graded asphalt (asphalt concrete) in that it has a higher asphalt/bitumen (binder) content, usually around 7–10% of the whole aggregate mix, as opposed to rolled asphalt concrete, which has only around 5% added asphalt/bitumen. This thermoplastic substance is widely used in the building industry for waterproofing flat roofs and tanking underground. Mastic asphalt is heated to a temperature of 210 °C (410 °F) and is spread in layers to form an impervious barrier about 20 millimeters (0.8 in) thick.

### 6.4 Asphalt Emulsion

A number of technologies allow asphalt/bitumen to be mixed at much lower temperatures. These involve mixing with petroleum solvents to form "cutbacks" with reduced melting point, or mixtures with water to turn the asphalt/bitumen into an emulsion. Asphalt emulsions contain up to 70% asphalt/bitumen and typically less than 1.5% chemical additives. There are two main types of emulsions with different affinity for aggregates, cationic and anionic. Asphalt emulsions are used in a wide variety of applications. Chipseal involves spraying the road surface with asphalt emulsion followed by a layer of crushed rock, gravel or crushed slag. Slurry seal involves the creation of a mixture of asphalt emulsion and fine crushed aggregate that is spread on the surface of a road. Cold-mixed asphalt can also be made from asphalt emulsion to create pavements similar to hot-mixed asphalt, several inches in depth and asphalt emulsions are also blended into recycled hot-mix asphalt to create low-cost pavements.

### 6.5 Other Uses

Asphalt/bitumen is used to make Japan black, a lacquer known especially for its use on iron and steel. Asphalt/bitumen also is used in paint and marker inks by some graffiti supply companies (primarily Molotov) to increase the weather resistance and permanence of the paint and/or ink, and to make the color much darker. Asphalt/bitumen is also used to seal some alkaline batteries during the manufacturing process.

## 7. FUTURE SCOPE

Naturally occurring crude Asphalt/bitumen impregnated in sedimentary rock is the prime feed stock for petroleum production from "Oil sands", currently under development in Alberta, Canada. Canada has most of the world's supply of natural asphalt/bitumen, covering 140,000 square kilometres (an area larger than England), giving it the second-largest proven oil reserves in the world. The Athabasca oil sands is the largest asphalt/bitumen deposit in Canada and the only one accessible to surface mining, although recent technological breakthroughs have resulted in deeper deposits becoming producible by *in situ* methods. Because of oil price increases since 2003, upgrading bitumen to synthetic crude oil has become highly profitable. As of 2006, Canadian crude asphalt/bitumen production averaged about 1.1 million barrels per day and was projected to rise to 4.4 million barrels per day by 2020.

Certain activist groups have become increasingly concerned about the global peak oil and climate change problem in recent years due to byproducts released into the atmosphere. Most of the emissions are derived primarily from burning fossil fuels. This has led to the introduction of petroleum alternatives, such as bioasphalt, that are more environmentally friendly and less toxic.

Asphalt/bitumen can now be made from nonpetroleum-based renewable resources such as sugar, molasses and rice, corn and potato starches. Asphalt/bitumen can also be made from waste material by fractional distillation of used motor oils, which is sometimes disposed by burning or dumping into landfills. Nonpetroleum-based asphalt/bitumen binders can be made light-colored. Lighter-colored roads absorb less heat from solar radiation, and have less surface heat than darker surfaces, reducing their contribution to the urban heat island effect.

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