

# **Adhesives from Creosote Bush (*Larrea tridentata*) Phenolic Resin with Formaldehyde. Characteristics and Application**

## **INTRODUCTION**

The governments of Mexico and the United States are individually and cooperatively planning and instituting programs in two important areas. The first involves the systematic assessment of indigenous plant species for economically useful raw materials, and the second involves actions to combat the destruction or desertification of vast land areas. The role of research and development, economic analysis, and modeling in the management and utilization of renewable natural resources cannot be overemphasized. A relatively small area (50,000 sq. mi.) of the Chihuahua desert has been chosen for our studies. The area is rich in naturally growing vegetable resources such as *Larrea tridentata*, also known as creosote bush. This shrub is an important renewable resource of the Chihuahua, Sonora, and Mojave deserts in North America. *Larrea divaricata*, which is considered conspecific with *Larrea tridentata*, is the dominant shrub in the Monte or central semidesert of Argentina.<sup>1</sup>

Recently, we characterized selected extracts of *Larrea tridentata* and found that they contain mainly substituted catecholic compounds called lignins, such as nordihydroguaiaretic acid (NDGA) and others. The extracts have a number-average molecular weight of 352 g/mole.<sup>2,3</sup> A study of the *Larrea* resin (and some derivatives) has been carried out and it was found that the resin is an acceptable antioxidant for rubbers and a potentially good antifungal agent for agricultural applications.<sup>2</sup> Therefore, a possible industrialization of the resin is being contemplated. We have also studied the polymerization of the resin with formaldehyde under different conditions and have characterized the resulting polymers.<sup>3</sup> This formaldehyde condensation reaction with lignins was found to be similar, as far as the type of products obtained, to the reported condensation of catechol, which reacts with formaldehyde under both acidic and basic conditions to give catechol methylols, their dimers and trimers with catechol, and finally high-molecular-weight condensation products.<sup>4,5</sup> Additionally, catechol has been reported to condense 2.3 times as fast as phenol with formaldehyde in aqueous solution in the presence of hydrochloric acid between 20 and 90°C.<sup>6</sup> In the presence of aqueous sodium hydroxide, catechol condenses with formaldehyde about 2.6 times faster than phenol.<sup>7</sup> It has also been reported that the amount of formaldehyde which condenses with catechol is at a minimum at pH 4.5. Consumption is accelerated by an increase or decrease in pH.<sup>8</sup>

In this note, we describe the characteristics and application for the new phenolic adhesive that results from the condensation of *Larrea* resin and formaldehyde.

## **EXPERIMENTAL**

### **Materials**

The one-step chloroform extraction of *Larrea* resin has already been described.<sup>2,3</sup> The yield of solvent-free phenolic resin is 8–10% (dry weight basis from leaves and twigs) with a softening point of 60°C. The hexamethylenetetramine was 99+% grade, melting point 280°C (sublimes) from Aldrich Chemical Co. (Milwaukee, WI). The paraformaldehyde (trioxymethylene) was the purified grade from Fisher Scientific Co. (Fair Lawn, NJ). Commercial phenol-formaldehyde resin (100% resin)-Novolac-type was obtained from Monomer-Polymer Labs (Philadelphia, PA). The Novolac resin is totally soluble in boiling absolute ethanol, but when the resin was heated for 10 min at 145°C it became totally insoluble in the same solvent. This fact shows that the resin is heat reactive and therefore contains residual active methylol groups.

### **Preparation of Adhesive Compositions**

The adhesive formulations are prepared by mixing the components shown in Table I. The formulations can be prepared as dry powders (indefinite shelf life) to be then applied appropriately to the wood. For testing purposes, the dry powders were applied to the wood with chloroform as a vehicle.

TABLE I  
Formulations for Adhesives that Incorporate *Larrea* Phenolic Resin

Component							
Composition No.	1	2	3	4	5	6	7
<i>Larrea</i> resin <sup>a</sup>	352	352	176	246	246	246	0
Hexamethylenetetramine <sup>b</sup>	140	70	70	70	35	14	5
Paraformaldehyde	60	45	15	15	15	24	0
Novolac resin (100%)	0	0	176	106	106	106	352
Wood flour, 100 mesh <sup>c</sup>	138	117	109	109	101	98	89

<sup>a</sup> Number-average molecular weight of 352 g/mole determined by vapor pressure osmometry (refs. 2 and 3).

<sup>b</sup> Theoretical molecular weight of 140.19 g/mole.

<sup>c</sup> Amount calculated to be 20% by weight of the total composition mix. Glue mix suspension in water had a pH of about 7.

### Preparation of Test Panels and Testing

Essentially the ASTM test methods D2339-65T and D906-64 were followed with some slight modifications. The methods are applied to determine the strength properties of adhesives in two-ply wood construction in shear by tension loading. The slight modifications were the use of chestnut veneer instead of sweet or yellow birch veneer and a moisture content of the test panels of 4–6% instead of 10–12%.

An Instron Tensile Tester model 1122 provided with suitable grips was used to determine the shear strength of the adhesives.

Triplicate plywood panels were prepared under the following conditions:

press temperature	145°C
pressure	280 psi (1.93 MPa)
pressing time	20 min
prepressing	none
adhesive spread	295 g/m <sup>2</sup> single glue line

The pressing time can be reduced to about 10 min if a formulation without organic solvent (chloroform) is used. The pressure, press temperature, and adhesive spread are similar to the conditions already reported in the literature.<sup>9</sup> After pressing, the plywood panels were cooled down at room temperature (23°C), conditioned, and then cut following the mentioned ASTM test methods. The pieces obtained were used to determine shear strength dry (ASTM), and after a 72-hr boiling water soak, following the British standards 1455 and 1088 for marine-grade plywood in which a rating from 0 to 100 is assigned (zero indicating complete glue failure and 100 complete wood failure), and stating that the average values for all glue lines tested shall not be less than 50% and no single glue line of less than 20% wood failure after boiling plywood samples in water for 72 hr. The South African 1971,<sup>10</sup> standard SABS929, for shear strength of marine-grade plywood has as its sole requirement that the test specimen present a shear strength of more than 200 psi after 72 hr of boiling.

### RESULTS AND DISCUSSION

The adhesive formulations were prepared in two different compositions. The first one involved the preparation of unfortified *Larrea* resin–formaldehyde adhesive and the second involved the preparation of fortified *Larrea* resin–formaldehyde adhesive. For this latter case a phenol-formaldehyde resin Novolac-type was used. The purpose for the addition of the Novolac resin was to improve the adhesive properties of the formulations. Because of their size and shape, the *Larrea* resin lignins become immobile at a low level of condensation with formaldehyde, so that the available reactive sites are too far apart for further methylene bridge formation. The result is incomplete polymerization and therefore lower values for the shear strength of the adhesive. A similar explanation has been given for the tannin–formaldehyde adhesives,<sup>9</sup> and in fact the problem has been corrected by adding bridging agents with longer molecules,<sup>9,11</sup> like phenolic or aminoplastic resins. These considerations are also in agreement with the work of Mark.<sup>12,13</sup> All this is experimentally corroborated with the data shown in Tables II and III for formulations that incorporate *Larrea* resin and from the determination of unpolymerized soluble *Larrea* resin in fortified compositions. Table

TABLE II  
Relationship between the Molecular Weight and the Softening Point for the Polymers of *Larrea* Resin with Formaldehyde

Molecular weight <sup>a,b</sup>	Softening point (°C)
352 ( <i>Larrea</i> resin)	60
498	65
668	100
727 (soluble portion) <sup>c</sup>	155 (total product)
1068 (soluble portion)	160 (total product)

<sup>a</sup> Number-average molecular weight (ref. 3).

<sup>b</sup> The molecular weights obtained are a function of the reaction time.

<sup>c</sup> The insoluble material (crosslinked) is about 15% of the total product. The solvent was reagent-grade dimethylformamide (DMF) at 100°C.

II shows the relationship between the molecular weight of the polymer and its softening point. The polymers become insoluble at a relatively low degree of polymerization and their softening point increases rapidly. To show that *Larrea* resin was being polymerized at a reasonable rate in the fortified formulations, we determined analytically the percent of soluble *Larrea* resin for fortified formulations. Chloroform was found to be a selective solvent for *Larrea* resin since it does not dissolve in any significant degree the other components of the formulation or even the *Larrea* resin-formaldehyde condensation dimers or trimers. In control tests of unheated formulations, the *Larrea* resin is extracted quantitatively. For thermally treated formulations (for example, formulation 3, Table I; 10 min at 145°C in test tubes) the amount of extracted *Larrea* resin was 30% for the finely grounded polymerized mass. This means that about 70% of the original *Larrea* resin had polymerized under the tested conditions. Unfortified *Larrea* resin would take a much longer time to arrive at 70% of insoluble material because of the relatively high softening point of the product even at a relatively low degree of polymerization<sup>3</sup> (see Table II). Therefore, for a possible high degree of polymerization of unfortified *Larrea* resin, the process temperatures for plywood manufacture would be unacceptably high. Table III shows that unfortified formulations (1 and 2) have a very low and unacceptable (for marine-grade plywood) shear strength dry, and also after a 72-hr boiling water soak. Their percent wood failure is zero (also unacceptable). However, the fortified formulations are acceptable in the mentioned properties. As a conclusion it can be said that since *Larrea* resin is a mixture of ring-substituted and O-substituted catechols, it is expected that the overall reactivity of the resin would be somewhat lower than unsubstituted catechol. However, our overall data shows that the reactivity of *Larrea* resin is still good enough to be considered as a partial effective replacement of Novolac resin in adhesive compositions instead of being only an active filler (extender) or even an unreactive plasticizer. The development of a pilot plant extraction process for *Larrea* resin, a five-year defoliation study of *Larrea* to avoid desertification, together with the availability, extent of distribution of *Larrea*, and also its unattended renewability, indicate that *Larrea tridentata*

TABLE III  
Plywood Shear Strength for Adhesive Formulations that Incorporate *Larrea* Resin

Composition No. <sup>a</sup>	Type of formulation	Shear strength ASTM			
		Dry		72-hr water boil	
		Strength (psi)	Wood failure (%)	Strength (psi)	Wood failure (%)
1	Unfortified	62	0	7	0
2	Unfortified	47	0	5	0
3	Fortified	510	100	258	90
4	Fortified	387	92	178	50
5	Fortified	337	93	192	40
6	Fortified	320	60	231	90
7	Novolac (control)	534	100	308	100

<sup>a</sup> From Table I.

will be in the near future an important source of raw materials instead of a pest, as it has been considered until now. These new applications for *Larrea* resin open an alternative source of renewable raw materials other than petroleum.

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