

Chapter 18

Condensed Tannins as Substitutes for Resorcinol in Bonding Polyester and Nylon Cord to Rubber

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Nylon and polyester cords used to reinforce tires are coated with a reactive resorcinol-formaldehyde-latex (RFL) adhesive dip to strongly couple the rubber and cord. Condensed tannins from pecan nut pith, bark of southern pine trees, or peanut skins can be used to replace some or all of the resorcinol in a standard RFL dip. When the tire cord adhesion test (TCAT) geometry is used, pullout forces for dipped nylon cords embedded in a typical styrene-butadiene rubber (SBR) vulcanizate nearly equaled those obtained with the standard dip when resorcinol was replaced with tannins from peanut skins or pine bark sulfite extracts. When bonding polyester cord, resins formulated with pecan pith sulfite extracts and purified pine bark tannins gave pullout forces substantially higher than the standard RFL dip. Resins made with peanut skin tannins or pine bark sulfite extracts as substitutes for resorcinol were marginally inferior to the standard RFL dip. When bonding to nylon cord, tannin preparations of low molecular weight appear to provide the stronger bonds. Bond strength was not influenced by the presence of sulfite ion or carbohydrates in nylon adhesion. Tannin preparations containing low proportions of carbohydrates gave the higher bond strengths in adhesion to polyester cord.

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Nylon and polyester cords are commonly used in tire body plies to impart strength and durability. To function properly, the cords must be firmly bonded to the surrounding rubber. Some coupling of cord to rubber occurs because of simple mechanical interlocking of rubber that has penetrated into the cord. However, this type of bonding is insufficient, and an adhesive interlayer is required. Typically, the cord fabric is dipped into a water-based adhesive, then dried before calendering into a rubber ply. The origin for the adhesives currently used dates to a patent by Charch and Maney (1). This class of adhesives is based on reactive mixtures of resorcinol, formaldehyde, and a rubbery latex (RFL) dips. A representative RFL composition (2) suitable for bonding nylon to a diene elastomer is detailed in Table I. In the adhesive, the resorcinol and formaldehyde react to form a product that reinforces the rubbery major portion (3). It is also the RF part of the adhesive that is thought to be principally responsible for the adhesive's strong interaction with the cord (4). During the vulcanization of a cord-RFL-rubber composite, co-curing across the rubber-adhesive interface is expected (5). One function of the pyridine moiety of the styrene-butadiene-vinylpyridine polymer is to increase the interaction between the latex rubber and the RF, thereby enhancing the cohesive strength of the dip (6).

Table I. Standard RFL-Type Adhesive Dip Composition

Component	Amount
Resorcinol	11 g
Formalin sol'n (37%)	16.4 mL
NaOH sol'n (10%)	3.0 g
Distilled water	236 g
Styrene-butadiene-vinylpyridine latex (41% solids)	244 g

The reactivity of resorcinol with formaldehyde is essential for developing the cohesive strength of the interlayer and its bonding characteristics. Condensed tannins are known to be very reactive with formaldehyde (7-9), so these renewable phenolic polymers are good candidates as resorcinol replacements. Indeed, condensed tannins from wattle and pine bark extracts have been successfully used in cold-setting, wood-laminating adhesives, and the former are used extensively in the commercial production of laminated timbers in South Africa (Pizzi, A., National Timber Research Institute, Pretoria, South Africa, personal communication, 1982) (10-13).

The purpose of the research described here was to explore the feasibility of using condensed tannins as replacements for resorcinol in RFL-type adhesive

dips for bonding of cord to rubber products. Success in this effort would greatly increase the markets for condensed tannins, since far more resorcinol is used in the rubber industry than in bonding of wood products.

Experimental Methodology

Materials. Two types of standard tire cord obtained from Gen Corporation were used in this investigation: polyester, 1300/3, and nylon 66, 1260/3. The rubber composition to which the adhesively dipped cords were bonded had the following composition in parts by weight: styrene-butadiene rubber (SBR) 1502, 100; N330 carbon black, 50; zinc oxide, 5; stearic acid, 0.5; sulfur, 1.7; 2-morpholiniothio-benzothiazole, 2. Master batches were mixed 7 min in a 350-ml Brabender Plasticorder, and curatives were added on a cool two-roll mill. Cure characteristics at 155 °C were determined with an oscillating disc rheometer (ASTM D 2084). The time to reach 90% of the final cure state was 23 min, and the Shore A hardness of the final vulcanizate was approximately 60.

Four types of condensed tannins were studied in the adhesive dips: 1) extracts from pecan nut pith obtained by digestion with aqueous sodium sulfite-sodium carbonate solutions, 2) purified tannins from southern pine bark, 3) extracts from southern pine bark obtained by digestion with aqueous sodium sulfite-sodium carbonate solutions, and 4) tannins extracted with acetone-water solutions from peanut skins.

The sulfite extract of the pecan nut pith was obtained by extracting the finely ground red powder (509 gm) with sodium sulfite (20.4 gm) and sodium carbonate (2.0 gm) in 2549 mL of water. Approximately 1 hr was required to reach reflux temperature, and the suspension was heated at reflux for 2 hr. The suspension was cooled, the volume adjusted to a constant by addition of water, and it was filtered twice through glass wool. Aliquots (100 mL) of the recovered liquor were freeze-dried to determine the extract yield. The remainder was also freeze-dried to recover a dark brown solid.

The purified pine bark tannin was obtained in the following manner. The phloem of freshly felled loblolly pine trees was removed by carefully peeling the outer bark away at the cork cambium and then peeling the white phloem from the xylem cambium. Strips of phloem were cut into sections of about 2 to 5 in² and immediately immersed in acetone-water (70:30, v/v). The extraction flasks were kept at ambient temperature, protected from exposure to light, for 48 hr, after which the solvent was recovered by filtration. The acetone was removed under vacuum on a rotary evaporator, and the aqueous solution was extracted four times with an approximately equal volume of ethyl acetate to remove low molecular weight phenolics. The remaining water-soluble extract was freeze-dried. Aliquots (about 50 gm) were redissolved in methanol-water (1:1, v/v), and the solutions were applied to 2.4 X 90 cm Sephadex LH-20 columns packed in this same solvent. The columns were eluted with methanol-water until no more colored material was eluted. The condensed tannin polymers absorbed

on the column packing were then eluted with acetone-water (50:50, v/v). The acetone was removed by evaporation under vacuum on a rotary evaporator, and the aqueous solution was freeze-dried.

The sodium sulfite-sodium carbonate extracts of pine bark were prepared from southern pine tree barks obtained from logs at a plywood plant in central Louisiana. The bark was collected from transfer chains immediately following the debarkers. After air-drying, the bark was first processed in a garden mulcher and then refined in a Sprout-Waldrin disk refiner fitted with breaker plates. The finely ground bark was divided into lots of approximately 30 lb (100 parts by weight), which were then extracted with 4.0 parts of sodium sulfite and 0.4 parts of sodium carbonate in 700 parts of water in a 40-gal capacity stainless steel tank. The solution was heated to 95 to 100 °C over 1 hr and maintained at temperature for 2 hr. The suspension was cooled, adjusted to a constant volume, and the extract liquor was filtered twice through fiberglass mats. Typically, 60% of the added liquor was recovered from the pulp. Approximately 100 gal of extract were dried in a hot pan evaporator.

For the preparation of the peanut skin tannin, the red skins were separated from residual nut and hull material by hand sorting, and then about 30 lb of skins were extracted with acetone-water (60:40 v/v) at a liquor-to-skins ratio of 5 to 1 at 50 °C for 4 hr in a stainless steel tank. The extract was filtered through a fiberglass mat, the acetone was removed under vacuum on a rotary evaporator, and the aqueous solution was freeze-dried.

Adhesive Preparation. The standard RFL dip that was used is given in Table I. In the dips containing the tannins, all ingredient amounts were held constant except the ratio of resorcinol to tannin. Starting with the control dip (Table I), tannin was simply substituted for resorcinol, such that dips containing resorcinol/tannin of 100/0, 75/25, 50/50, 25/75, and 0/100 were prepared as follows. Resorcinol, tannin, formalin, NaOH solution, and distilled water were mixed together and allowed to react for 2 hr. Then, the styrene-butadiene-vinyl pyridine latex (Gentac 118 from Gen Corporation) was added, and the dip was allowed to age 24 hr before use. In some cases, the adhesive became a soft gel. This, however, could be "broken" by mixing, and it was still possible to coat the dip onto the test cord. The dip was applied to a cord by immersing the cord in the dip for 30 s. The cord was then removed and dried 5 hr at room temperature before preparing pullout test specimens. In industry, a short heat treatment after dip application is often employed, however, this was not done in the present investigation.

Pullout Tests. The method to determine the adhesion between the dipped cords and the SBR vulcanizate was the tire cord adhesion test (14,15), Figure 1. Here, two cords are embedded (to a depth of 10 mm) into opposite ends of a rubber block (76 mm x 13 mm x 6.4 mm). Samples are then cured 23 min at 155 °C and allowed to rest 1 day. Bond strengths are determined by clamping the two free cord ends in an Instron and pulling at the rate of 50 mm/min.

Failure occurs when one of the cords is pulled-out; the strength is denoted by the maximum force during cord pullout.

Results and Discussion

In the presentation of data and discussion that follows, the four types of condensed tannin extracts are designated: pecan pith sulfite extract (1), purified pine bark tannin (2), pine bark sulfite extract (3), and peanut skin tannin (4). Pullout strengths for the polyester and nylon cords coated with dips containing the four tannins are given in Figures 2 to 7. All data points are the average of six pullout forces. Pullout forces as a function of percent resorcinol (based on the total of resorcinol and tannin) in the dip are given in Figures 2 and 3 for the polyester and nylon cord, respectively. The rightmost data points are values for the control dip containing no tannin. It is worthwhile to note first that many of the dips containing the condensed tannins had pullout strengths nearly equal to or exceeding those of the control containing only resorcinol. This is especially true with the polyester cord.

The type of tannin markedly influences the pullout force. With the polyester cord, the highest pullout force was obtained with a dip containing 25/75, resorcinol/pecan pith sulfite extract. However, this same dip gave among the lowest strengths when applied to the nylon cord. On the other hand, quite good bonding to nylon was obtained with a 50/50, resorcinol/peanut skin tannin dip, while this composition led to a quite low pullout force with the polyester cord. A comparison between the behavior of nylon and polyester with the various dips is better shown in Figures 4 to 7, where pullout forces for each of the four types of tannin-containing dips are presented. Generally, the pecan pith sulfite extract and purified pine bark tannin give superior results with polyester cord, whereas, just the opposite is true for the pine bark sulfite extract and the peanut skin tannin.

The tannin extracts examined in this preliminary study represent a wide range of properties. For example, both the peanut skin and purified pine bark tannin extracts are predominantly polymeric procyanidins (3,5,7,3',4'-penta-hydroxyflavans), but the peanut skin tannin is much lower in molecular weight (16-19). In bonding to nylon, the resins formulated with peanut skins performed much better than those made with purified pine bark tannins. The condensed tannins from pine bark undergo interflavanoid bond cleavage with the formation of flavan- or procyanidin-4-sulfonates when reacted with sulfite ion (20); so, even though experimental evidence is lacking for the molecular weight of sulfite extracts of bark, it seems probable that the sulfite extracts from pine bark are of a lower molecular weight than the purified tannins.

The sulfite extract performed nearly as well as the peanut skin tannin in bonding to nylon. Use of a tannin sulfonate derivative does not seem to hinder the development of strong bonds (compare peanut skin and sulfite extracts from pine bark). Likewise, the presence of carbohydrates in the tannin extracts does

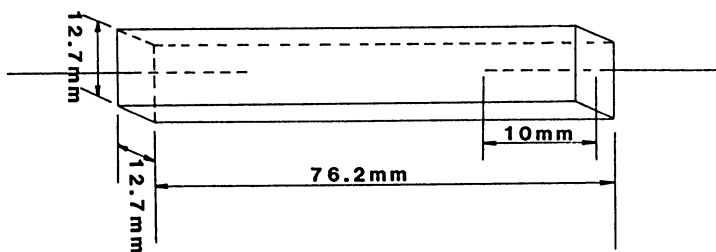


Figure 1. TCAT pullout test geometry.

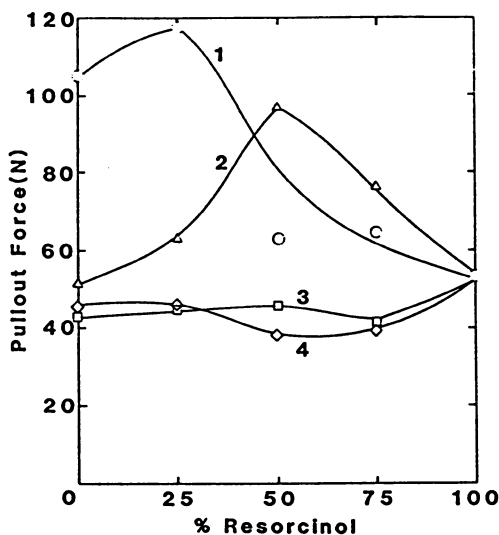


Figure 2. Pullout forces of polyester cords for various tannin-containing adhesive dips as a function of percent resorcinol. 1, pecan pith sulfite extract; 2, purified pine bark tannin; 3, pine bark sulfite extract; 4, peanut skin tannin.

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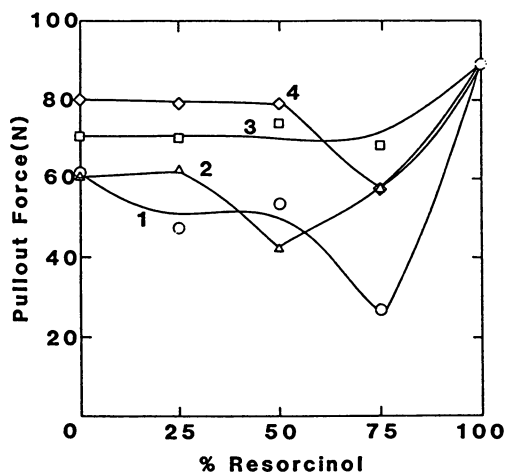


Figure 3. Pullout forces of nylon cords for various tannin-containing adhesive dips as a function of percent resorcinol. Designation same as Figure 2.

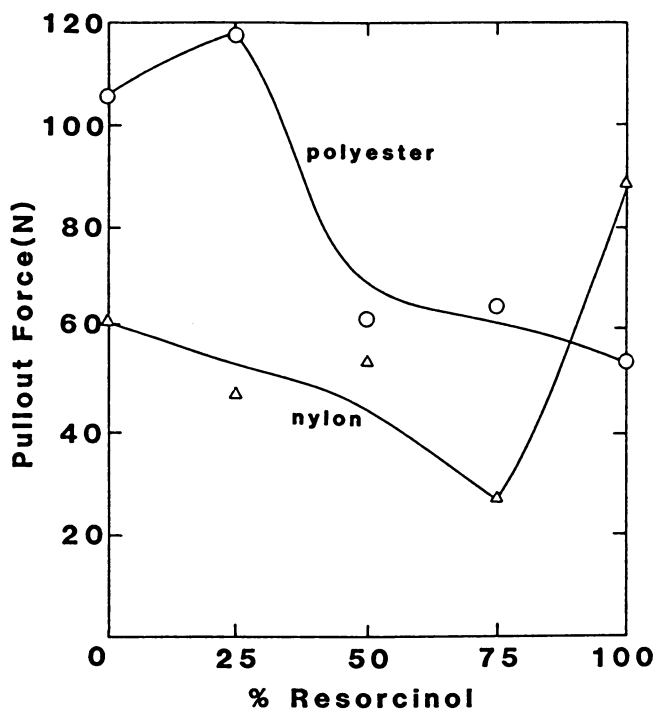


Figure 4. Comparison of the pullout forces of polyester and nylon cords for dips containing pecan sulfite extract.

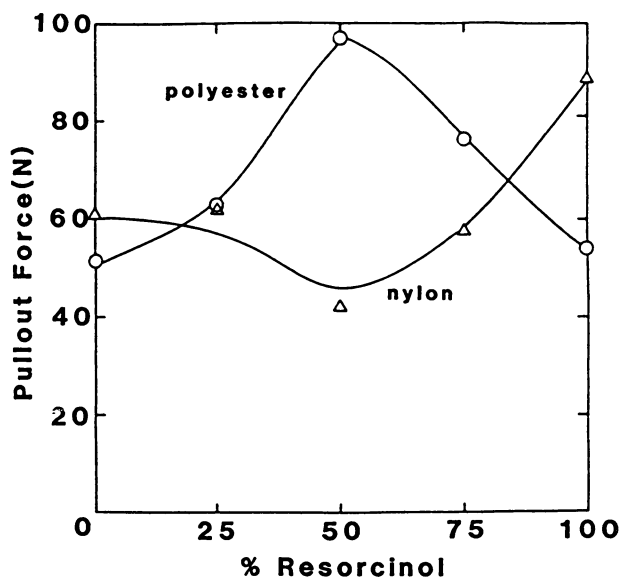


Figure 5. Comparison of the pullout forces of polyester and nylon cords for dips containing purified pine bark tannin.

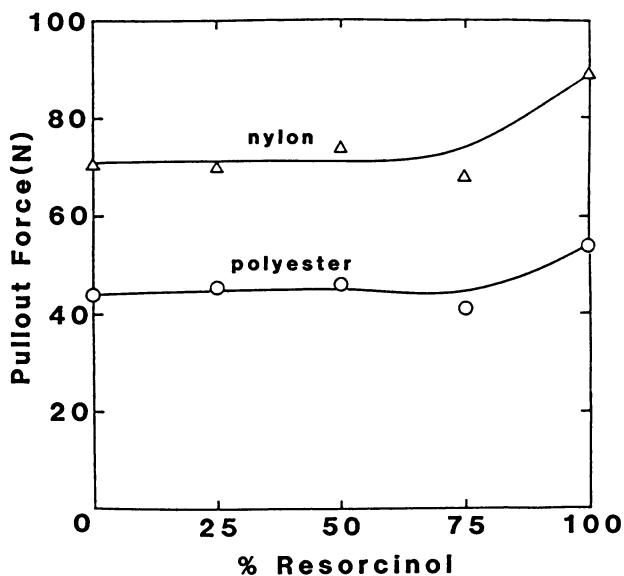


Figure 6. Comparison of the pullout forces of polyester and nylon cords for dips containing pine bark sulfite extract.

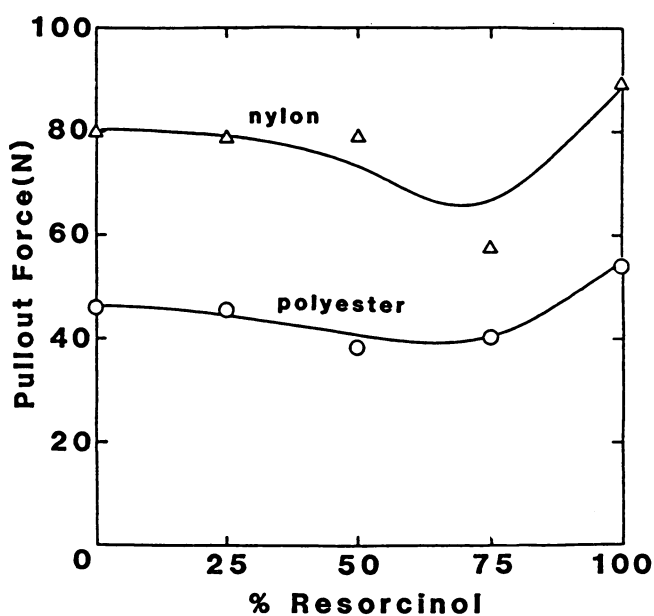


Figure 7. Comparison of the pullout forces of polyester and nylon cords for dips containing peanut skin tannin.

not seem to reduce bond strength. The purified pine bark extract contains no measurable amounts of carbohydrates, whereas, the extracts from peanut skins and sulfite extracts from pine bark contain between 15 and 20% of co-extracted carbohydrates.

At this time, it is not possible to pinpoint the reason for the poor performance of the pecan pith extract in bonding to nylon. The tannin is predominantly a prodelphinidin (3,5,7,3',4',5'-hexahydroxyflavan) instead of procyanidin (Hemingway, R. W., Southern Forest Experiment Station, unpublished results), but that would not seem to be a reasonable cause for such a large difference in behavior. A comparison of elemental composition and carbohydrates obtained after hydrolysis shows much lower amounts of carbohydrates in the pecan pith extract (Table II). The low proportion of carbohydrate obtained after hydrolysis is consistent with comparatively high Stiasny polyphenol content of 87% for the pecan pith extract.

Table II. Elemental Composition and Carbohydrate Content of Sulfite Extracts from Pecan Nut Pith and Southern Pine Bark

Property	Pecan	Pine
Yield		
Percent of dry weight	52	18
Elemental Composition		
Carbon	46.2	45.4
Hydrogen	4.4	4.7
Sodium	7.2	5.8
Sulfur	4.4	3.8
Carbohydrates		
Glucose	—	4.9
Xylose	4.5	2.4
Galactose	0.7	4.5
Arabinose	—	3.0
Mannose	1.4	4.4
Total sugars after hydrolysis	6.6	18.2
Stiasny polyphenols	87	52

The pecan pith extract was the best of the tannin extracts examined in bonding to polyester cord. Pullout forces using this extract to totally replace resorcinol were nearly twice as high as in the standard dip. The purified pine bark extract also gave very good results. One commonality in these two extracts

was the low proportion of carbohydrates. Bond strengths to polyester cord using resins based on peanut skin tannins and pine bark extracts obtained by extraction with sodium sulfite were about the same and only marginally lower than those obtained using the standard RFL dip. As was noted in bonding to the nylon cord, sulfonation seems to have little influence on bond strength. These types of extracts have also proven to be good resorcinol substitutes for cold-setting, wood-laminating adhesives. Even though the extracts carry sulfonic acid functions, durable water-resistant bonds are produced (19,21). The results with the polyester cord are particularly encouraging, since the simple RFL control dip is not that well suited for greige polyester cord. It should be noted that this research effort has made no attempt to optimize the formulation of dips containing condensed tannins. Rather, the procedure for the dip modification was a simple substitution by weight of tannin for resorcinol. The ratio of ingredients is expected to greatly influence viscosity, cure rate, and pH, as well as the bonding characteristics. In a patent search following this preliminary work, a 1967 Japanese patent (22) was discovered that had not been previously noted. The influence of type of tannin extract or modifications in resin formulation were not disclosed in this patent either. Therefore, additional studies to examine these effects are planned. This additional work will hopefully allow a better understanding of the bonding properties that will lead to improved strength and durability of adhesion of cord to rubber matrices.

Conclusions

Condensed tannins have considerable promise as substitutes for resorcinol used in resin formulations for bonding of nylon or, particularly, polyester cord to rubber. Although much more work needs to be done, preliminary results suggest that refinement of extract properties and adhesive formulations could lead to a large, high-value market for condensed tannin extracts.

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Literature Cited

1. Charch, W. H.; Maney, D. G. U.S. Patent 2 128 299, 1938.
2. Doyle, G. M. *I.R.I. Transactions*. 1960, **36**, 177.
3. Moul, R. H. In *Handbook of Adhesives*; Skeist, I., Ed.; Van Nostrand Reinhold: New York, 1977, pp 661-688.

4. Iyenger, Y. J. *Appl. Polym. Sci.* 1978, **22**, 801.
5. Takeyama, T.; Matsu. *J. Rubber Chem. Technol.* 1969, **42**, 159.
6. Reeves, L. N. *Rubber World.* 1955, **132**, 764.
7. Pizzi, A. In *Wood Adhesives: Chemistry and Technology*; Pizzi, A., Ed.; Marcell Dekker: New York, 1983, pp 177-246.
8. Hemingway, R. W.; McGraw, G. W. *J. Liquid Chrom.* 1978, **1**, 163.
9. Kiatgrajai, P.; Wellons, J. D.; Gollub, L.; White, J. D. *J. Org. Chem.* 1982, **47**, 2913.
10. Pizzi, A.; Rossow, du T.; Knuffel, W. E.; Singmin, M. *Holzforschung und Holzverwertung.* 1980, **32**, 140-150.
11. Pizzi, A.; Cameron, F. A. *Forest Prod. J.* 1984, **34**, 61-68.
12. Kreibich, R. E.; Hemingway, R. W. *Forest Prod. J.* 1985, **35**, 23-27.
13. Kreibich, R. E.; Hemingway, R. W. *Forest Prod. J.* 1987, **37**, 43-46.
14. Nicholson, D. W.; Livingston, D. I.; Fielding-Russell, G. S. *Tire Science and Technology.* 1978, **6**, 114.
15. Hamed, G. R.; Donatelli, T. *Rubber Chem. Technol.* 1983, **56**, 450.
16. Karchesy, J. J.; Hemingway, R. W. *J. Agric. Food Chem.* 1980, **28**, 222-228.
17. Hemingway, R. W.; Foo, L. Y.; Porter, L. J. *J. Chem. Soc. Perkin Trans. I* 1982, 1209-1216.
18. Williams, V. M.; Porter, L. J.; Hemingway, R. W. *Phytochemistry* 1983, **22**, 275-281.
19. Karchesy, J. J.; Hemingway, R. W. *J. Agric. Food Chem.* 1986, **34**, 966.
20. Foo, L. Y.; McGraw, G. W.; Hemingway, R. W. *J. Chem. Soc., Chem. Commun.* 1983, 672-673.
21. McGraw, G. W.; Laks, P. E.; Hemingway, R. W. *J. Wood Chem. Technol.*, in press.
22. Matsushita, T. Japanese Patent 8227/67, 1967.

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