

Tung Oil Research and Development at the Southern Regional Laboratory¹

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Abstract

This paper reviews utilization research on tung oil conducted at the Southern Regional Research Laboratory in New Orleans. The tung oil program began with the inception of the Laboratory in 1940. Utilization research on tung oil has been concerned with exploratory chemical reactions to develop new or improved industrial products and with the development of improved paint formulations. The emphasis of the domestic and foreign extra-mural program supervised by this Laboratory has been aimed at the practical applications of tung oil in plastics and the effects of heat on tung oil. Accomplishments over the past few years in these areas are described, and some projections for future research needs are proposed.

Introduction

DURING THE 25 YEARS that the U.S. Department of Agriculture has been engaged in utilization research on tung, objectives have been modified to meet radical changes in market conditions. When the tung industry was established in this country, about 1930, paints and other protective coatings were based almost entirely on oils, and tung held an apparently secure market position because of its excellent properties as a drying oil. At that time modern methods of handling and processing were unknown.

Today, production of tung oil has been modernized, a development to which the Department of Agriculture research has made many contributions. Unfortunately, at the same time, synthetic resins have replaced natural oils to a great extent, and indications are that the trend will continue. Most recent efforts have been directed toward finding new uses for tung oil and its derivatives and in developing improved products to maintain its position in conventional fields of utilization.

During the early years, much attention was given to determining the effect of cultural factors, such as soil and fertilizer, on the contents, quality, and physical and chemical characteristics of the oil in tung fruit.

Effects of various methods of drying tung fruit and the hulled nuts and meal, and of various conditions of storage were studied in order to define conditions for the minimum deterioration of oil. A new procedure for hulling the moist fruit in the field was found to minimize oil losses in the hulling process. Effects of moisture and shell in tung meal and of preheating the meal on the efficiency of tung oil expressions were investigated, as was the efficiency of various solvents and their effect on oil quality in solvent extraction. Some work was done on the use of tung meal in animal feeds after treatment to reduce toxicity. Methods for sampling and analyzing the tung seed for moisture and oil content were developed which are now in use in the tung industry. Methods of analysis were also

devised to determine the quality of tung oils and their content of *alpha*- and *beta*-eleostearic acids.

In an effort to extend utilization of tung oil into new fields, research was also directed in the early years toward the development of chemical derivatives which would find application in resins, plastics, and other synthetic materials. Extensive studies were undertaken on the chemical structure and reaction of eleostearic acids. Adducts were prepared by the Diels-Alder reaction with maleic anhydride, *beta*-propiolactone, acrylonitrile, and fumaronitrile and were tested as plasticizers for vinyl resins.

Some protective coatings prepared with tung oil fatty acids and epoxy resins showed excellent qualities in early evaluations, with good color and resistance to water, alkalis, and organic solvents, with high gloss and good mar resistance, and with unusual properties of adhesion. In the preparation of paints and varnishes, the tendency of tung oil to gel during cooking has been a handicap. During investigations on the preparation of coatings it was found that this tendency can be controlled by the addition of zinc resinate. Further, the excess drying capacity of tung oil can be turned to advantage by introducing nondrying but potentially fungicidal acids in protective coatings to provide built-in resistance to damage from mildew and other fungi. The work has been reviewed in a bibliography covering 20 years of tung utilization research (11).

Nature of More Recent Programs

More recently the research at the Southern Utilization Research and Development Division has been conducted along four lines: fundamental studies on the chemistry of the major constituents of tung oil; new formulations and derivatives of utility as fire-retardant protective coatings, agricultural chemicals, surfactants, or plasticizers; incorporation in alkyd resins; and detoxification of tung meal. The major effort however has been in the field of protective coatings, traditionally the largest market for tung oil.

Chemical Derivatives of Tung Oil

To extend the utilization of tung oil and improve its economic status, chemists at the Southern Regional Research Laboratory have been engaged in research on the development of new chemical derivatives of the oil which may find application as industrial products.

The chief constituent of tung oil is the glyceride of *alpha*-eleostearic acid, a straight-chain, 18-carbon fatty acid that contains a conjugated triene system. *alpha*-Tung oil or its component *alpha*-eleostearic acid may be readily converted to the *beta*-isomer, which also contains a conjugated triene system. Tung oil normally contains about 78% of eleostearic acids together with small percentages of other fatty acids such as oleic, linoleic, and stearic.

The very active systems of double bonds in eleostearic acid react in a readily predictable fashion with a great number of different organic compounds by the Diels-Alder reaction. This particular reaction has been used to advantage in preparing new chem-

¹ Presented at AOCs Meeting, New Orleans, May 1967.

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ical derivatives of tung oil for use in the manufacture of plastics. As part of this program, research was conducted on the isomerization of *alpha* to *beta* tung oil, preparation and determination of the chemical structures of highly pure eleostearic acid, alcoholysis of tung oil for the production of various esters, and the reaction of these materials with maleic anhydride, *beta*-propiolactone, acrylonitrile, and fumaronitrile as dienophiles. Data have been obtained on the ester adducts as plasticizers of vinyl resins. Briefly to summarize, formulations containing the esters of the maleic anhydride-*beta*-eleostearic acid adducts gave higher tensile strength values to vinyl resin than dioctyl phthalate. Butyl diesters of the acrylic acid, *beta*-eleostearic acid adducts are decidedly superior from the standpoint of low-temperature plasticizing characteristics to dioctyl phthalate. Both the butyl *alpha* and butyl *beta*-eleostearate acrylonitrile adducts are satisfactory secondary plasticizers when incorporated with ether dioctyl phthalate or tricresyl phosphate (6).

Several methods for the preparation of tung oil monoglycerides have been developed. Products richest in both monoglyceride and triene conjugation have been obtained by glycerolysis with sodium methoxide in pyridine solutions. Monoglycerides have been effective in lowering the surface tension of water as well as the interfacial tension of several oils, including tung oil, against water. Tung oil monoglycerides behaved as fugitive emulsifiers and, after drying, retarded the removal of spray residue by washing with a water spray more than did other emulsifiers, such as cottonseed oil monoglycerides (12). This method of preparing tung monoglycerides was scaled up to a pilot basis, and preparations using from 30-47 lb of tung oil produced a product containing from 32-45% tung monoglycerides. In addition, ammonium soaps of eleostearic acids were prepared, and they also acted as fugitive emulsifiers (1).

To extend the utilization of tung oil and to make available a new source of raw material, research has been directed toward the development of new chemical derivatives suitable as plasticizers or softeners for nitrile rubbers. Eight derivatives of tung oil, namely, the adducts of methyl vinyl ketone, dimethyl maleate, methyl acrylate, and acrylonitrile and their hydrogenated products, were prepared and screened as softeners with dibutyl sebacate as the control. In all cases the stocks prepared from the unhydrogenated derivatives were superior in plasticizing efficiency to those prepared from their hydrogenated counterpart or to those prepared from the control. Three of the unhydrogenated adducts yielded stocks that met the low-temperature flexibility requirements of the automotive industry (7,14).

In addition, four divinyl sulfone eleostearate adducts were synthesized and compared with dibutyl sebacate as plasticizers for nitrile rubber. Three of these, the adducts of methyl *alpha*-eleostearate, its hydrogenated derivative, and that of tung oil, were found to be satisfactory primary plasticizers. As in the case of the previous experiments, the stocks prepared from the unhydrogenated adducts were superior in plasticizing efficiency to those prepared from their hydrogenated derivatives. The divinyl sulfone tung oil adduct also yielded a rubber which met the low temperature flexibility requirements of the automotive industry (15).

A research project on tung oil under Public Law 480 has been granted to the Organic Chemistry Divi-

sion of the National Chemical Laboratory of India. The project specifically covers a study of the effects of heat on tung oil and its derivatives in the absence of air, as related to time intervals and temperatures of heating. The compounds formed are being separated and purified, and their structure and characteristics are being determined. Sukh Dev, the principal investigator, and his co-workers during the past year have definitely proved the chemical structure of the cyclic monomer, thus formed by heating methyl eleostearate from tung oil, to be methyl 5-butyl 1,3-cyclohexadiene-6-caprylate. In further heating, the double bonds of this monomer migrate to other positions, forming compounds of different structures. A catalytic method for greatly increasing the yield of the cyclic monomers has also been developed.

Tung Oil Coatings

Fire-Retardant Coatings

In recent years the research on tung oil coatings has principally been in the area of water-resistant tung oil containing intumescent fire-retardant coatings. The development and proper application of good fire-retardant surface coatings has been strongly recommended by coating technologists, fire marshals, and industrial and government officials to reduce the loss through fire of life and property. The National Safety Council reported that, in 1965, property destroyed by fire in the United States amounted to \$1.455 billion.

There have been misconceptions however about the purposes of fire-retardant coatings. Although they do not prevent fires, they do temporarily suppress the spreading of flames. By permitting fire-fighters to arrive at the scene before the building is engulfed by flames, this temporary delay could help save many lives. Since there are millions of nonfire-resistant buildings throughout the country, effects of fire-retardant coatings would have unlimited military and industrial potential.

In addition to being fire-retardant, these coatings should have the serviceable, protective, and esthetic properties of conventional coatings, such as can-stability, spreadability, drying and bonding characteristics, color and tint retention, serviceability, and water- and weather-resistance. None of the fire-retardant coatings presently available commercially possess all of these desired characteristics (16).

Fire-retardant coatings vary in performance, but, generally speaking, there are two types: intumescent and nonintumescent. The intumescent types are more common and appear to be more effective since their foaming expansion insulates the substrate from the effects of heat and flames and reduces the spread of fire. Two types of components promote this protective action: spumifics, which foam; and carbonifics, which produce a carbon matrix. Their combined response creates layer upon layer of spongelike, insulating mats of cellular, carbonaceous material. The components that produce the best spumific and carbonific action however appear to be too water-sensitive to be used in reliable fire-retardant coatings. Since commercially available, intumescent fire-retardant coatings did not meet all military requirements, the Southern Regional Research Laboratory undertook a cooperative research program with the U.S. Army Engineer Research and Development Laboratories to develop better coatings based on tung oil.

The unique chemical structure of tung oil with its

conjugated triene moieties appears to promote the synthesis of oil-based vehicles which have good drying and bonding characteristics, serviceability, water- and weather-resistance (21).

But, perhaps of greatest importance, these tung-oil containing vehicles appear to act synergistically with the spumific and carbonific components, additives, and pigments to produce the desired foaming, intumescent structures when exposed to heat and flame. In addition, highly water-resistant, carbonific penta-erythritol polyurethanes were synthesized with various percentages of pentaerythritol, toluene di-isocyanates, and phenyl isocyanate or pentaerythritol and toluene di-isocyanate. These pentaerythritol polyurethanes are easily pulverizable to light-colored powdery material, which is readily formulated into experimental fire-retardant coatings. Highly water-resistant spumific melamine phosphates were also synthesized, and these too are readily pulverized and formulated into coatings.

The three major coating components, i.e., the tung oil-containing vehicle, the spumific and carbonific components were formulated along with pigments and additives to produce water-resistant intumescent, fire-retardant coatings which exhibit satisfactory fire-retardant performance in the Underwriters' Laboratories (UL) tunnel furnace.

For comparative purposes fire-retardant coatings were formulated with oil-based vehicles free of tung oil, but, in all cases, these coatings were inferior to the tung oil containing fire-retardant coatings. The U. S. Army Engineer Research and Development Laboratory has recently indicated that specifications are being prepared on the basic formulas developed at the Southern Regional Research Laboratory (17,18).

In the course of the research on coatings which would exhibit satisfactory fire-retardant performance in the UL tunnel furnace, the importance of developing a day-to-day screening technique was recognized. Acceptable coatings would be required to exhibit satisfactory fire-retardancy in the Underwriters' Laboratories 25-foot tunnel furnace (ASTM E84-61) before fire marshals and government officials would recommend their use. In addition, it became apparent that the small laboratory screening test, such as the standard fire-test cabinet (ASTM D1360-58), did not provide a meaningful appraisal of experimental coatings prior to their final evaluation in the UL tunnel furnace. To bridge the gap between the mild but informative fire-test cabinet and the severe UL tunnel furnace test, an elementary 16-foot tunnel furnace was designed to simulate some of the conditions observed in the larger UL tunnel furnace.

With this day-to-day screening technique it was possible to expedite the development of fire-retardant coatings which would exhibit low flame-spread and fuel-contributed index values in the UL tunnel furnace. The intumescent fire-retardant performance of the experimental coatings in the elementary SU 16-foot tunnel furnace and in the UL 25-foot tunnel furnace correlated so well that relatively few experimental coatings required evaluation in the much larger UL tunnel furnace since it was considerably easier and faster to evaluate experimental coatings in the SU 16-foot tunnel furnace than in the UL 25-foot tunnel furnace. A substantial saving in valuable research time and direct testing costs was achieved (19,20).

An Isophthalic Tung Oil Alkyd Vehicle

Oil-modified alkyds are usually prepared by alcoholizing a glyceride oil with a suitable polyol and subsequently reacting the resulting hydroxy esters with a suitable dibasic acid. When tung oil is used, special precautions must be taken: first, to insure that a sufficiently high temperature has been attained during processing for gas-proofness and, second, to avoid gelation of eleostearic acid at gas-proofing temperatures. It was found that gas-proof, tung oil isophthalic alkyds of long oil contents can be prepared quite satisfactorily if the tung oil is alcoholized with such polyols as trimethylolethane, trimethylolpropane, or pentaerythritol at gas-proofing temperatures of about 300°C instead of the lower temperatures commonly employed for alcoholysis of glyceride oils. It appears that, in the presence of excess hydroxyl which prevails during alcoholysis, the tendency of the tung oil to gel is greatly reduced (4).

Epoxy Resin Esters Containing Tung Oil Fatty Acids

Methods have been devised for the incorporation of tung oil fatty acids in typical epoxy resin esters. These esters retain about half of the conjugated triene originally present in the tung oil derivatives which are used. The products show the outstanding adhesion, high chemical resistance, unusual flexibility, and extreme hardness usually associated with esters derived from epoxy resins and long-chain fatty acids. They generally dry more rapidly and require less dryer. The films show greater hardness and greater resistance to water and strong organic solvents; however, after baking at higher temperatures, they are somewhat less flexible and darker in color than the best products obtained from corresponding esters made with other long-chain fatty acids (5). Use of zinc resinate as an esterification catalyst reduces the time required for esterification and hence the danger of gelation, also results in improved wetting properties and markedly improved resistance of films to aqueous alkalis. Titanium dioxide, melamine, and flush colors may be incorporated to provide films of usual adhesion, glass, mar-resistance, and depth of color. Potentially fungicidal acids, such as propionic acid or undecylenic acid, may be incorporated in the esters, some of which retard mildew growth (3).

Varnish and Varnish Type of Vehicles

A tung-oil resin varnish vehicle was produced from tung oil and rosin by a process which made use of the polymerization-inhibiting quality of zinc resinate. Zinc resinate inhibits the uncontrolled gelation of eleostearic acid at gas-proofing temperature; however it produces coatings that require an excessively long time to dry. With the incorporation of rosin, the drying time has been reduced to 3-5 hr. To develop this product and to process and establish optimum processing conditions for commercial production, large-scale pilot-plant evaluations were undertaken. A tung-oil varnish vehicle formulation consisting of 66.7% of tung oil, 13.3% of zinc resinate, and 20% of maleic modified rosin ester was cooked successfully in closed, liquid-heated vessels of commercial size. With this formulation, reflux of the volatiles given off by the cooking varnish was essential to the prevention of gelling if the total cooking time employed exceeded about 4.5 hr. By varying the length of cooking time and the conditions of reflux under which cooking is done, varnishes varying in viscosities from 1.8 Stokes to 300 Stokes (50% solids content) can be produced.

In addition, the drying time of the varnishes produced can be controlled to some extent by controlling the time of cooking and by the use or nonuse of volatile reflux (2).

Utilization of Tung Meal

Tung meal is highly toxic to animals, including man, and has found little use except as a nitrogenous fertilizer. However it contains as much as 25-30% crude protein as it comes from the screw presses of a tung mill and is a potentially valuable feedstuff. A review of the literature shows that there are at least two types of toxic substances in the tung kernel. One of these is insoluble in organic solvents and is easily detoxified by heat. The second is extractable by ether, ethanol, and many other organic solvents (but not by petroleum ether) and is comparatively heat-stable. Research at the Southern Regional Research Laboratory has shown that two nitrogen-free toxins could be separated from this soluble material by chromatographic procedures (9).

Chick-feeding tests were used to determine which fraction was toxic at every separation. Both substances were highly toxic as 10-mg doses killed four-day-old chicks. These substances were shown by paper chromatography to be different and chromatographically homogeneous but also unstable. The elementary composition, hydroxyl contents, saponification values, and specific rotations for the two toxins were determined. Based on limited chemical and physical data, including the infrared and ultraviolet spectra of the toxins and their saponification products, it is suggested that these toxins are diesters of a 2,3-unsaturated-5-keto acid, a polyhydroxy acid, and a 3,4-unsaturated-5-keto tertiary alcohol. The 2,3-unsaturated-5-keto acid is assumed to be in equilibrium with its enol tautomer; the keto form with a conjugated diene and the enol form a conjugated triene structure. The polyhydroxy acid appears to be similar to gluconic acid (13).

In attempts to detoxify tung meals, batches were treated with gaseous ammonia at 100 psi at room temperature, at 110C, also at 110C with phosphoric acid, with sodium carbonate, and with urea, also by benzene extraction. The treated meals were fed to chicks by replacing half the protein in a standard chick ration by protein from the tung meal. All treatments except benzene extraction greatly reduced toxicity of the meal. But no ration containing tung meal was equal to the standard chick ration in its effect on rate of growth (10).

Calf-feeding tests were also carried out on treated tung meal. One meal was ammoniated, and the others were treated at different levels of phosphoric acid content. These studies showed that the gross efficiency of utilization was poor and the consumption lower than control rations. It was found that the ammoniated tung meal was more efficiently utilized than either of the phosphoric acid-treated meals (8).

Future Research

Objectives in utilization research on tung are to develop basic information about reactions, characteristics, properties of tung oil, tung meal, and their

components and to conduct research on the application of these findings to improve the economic value of tung. In speculating on the potential of tung, it is quite obvious that the chemical industry offers a particularly inviting field for research to increase tung oil utilization. Billions of pounds of synthetic organic chemicals are produced annually for use in plastics, plasticizers, lubricants, surface-active agents, and agricultural chemicals. This is a rapidly expanding market area where new chemicals form tung oil or eleostearic acid should find a place.

One of the real problems of research is to find the proper application for a new chemical based on its properties and cost. For example, further investigations of the preparation and properties of the Diels-Alder adducts of dienes containing eleostearic acid should provide more useful compounds; the glycidyl and aziridinyl type of monomers should provide valuable polymers and copolymers of industrial importance; methylol derivatives, by the addition of formaldehyde to eleostearic acid or its esters, should provide interesting base products for such reactions as epoxidation, acetylation, and hydrogenation to give useful plasticizers or rubber softeners; divinyl sulfone derivatives or esters of sucrose could lead to interesting applications; nitriles of the monoglycerides and its polymers should find a valuable and interesting use in lubricating oil additives; the products of oxidation should yield many new and valuable compounds. Thus, tung oil seems to offer unlimited opportunities as a useful intermediate upon which to build a whole new class of profitable industrial chemicals.

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[Received July 3, 1967]