

The Use of Drying Oils in Oleoresinous Varnishes

JOHN M. HAFELI, Reichhold Chemicals Inc., Chicago, Illinois

DRYING oils are the essential ingredients in three major types of protective coatings — enamels, paints, and varnishes. The first type can be further classified into those enamels which are made with varnish vehicles and those which are formulated with oil modified synthetic condensation resins known as alkyds. An earlier lecturer discussed these synthetic products in detail, and the importance of oils in paints was emphasized in the discourse which preceded this period. It will be the purpose of this talk to outline the importance and use of drying oils in varnishes, with special emphasis given to the relationship of the oil employed to the intended use of the varnish as an individual coating or as one of the principal vehicles in an enamel or other protective coating.

The origin of the word "varnish" is buried in legend, and the differences of opinion which have been expressed in the past make it difficult to give any accurate explanation. The technical societies are also reluctant to give a universally accepted definition of a varnish, but the most accurate is the one repeated in "Protective and Decorative Coatings, Volume III," by J. J. Mattiello: "A liquid coating material containing no pigment which flows out to a smooth coat when applied and dries to a smooth, glossy, relatively hard, permanent solid when exposed in a thin film to air."

From a chemical standpoint, and based on their constituents, varnishes are heterogeneous systems of two types:

- a) Spirit
(Resin and thinners)
- b) Oleoresinous
(Resins, oils, thinners, and driers)

Physically, as given in the definition, they are fluids which can be spread easily to smooth films which dry to hard, continuous, solid coatings when allowed to dry in the air or when exposed to heat. The solvent or thinner is fundamentally a carrier for the solid portion of the system, and it evaporates into the atmosphere. The solid portion then dries by oxidation and/or polymerization-condensation reactions. Those which dry by evaporation only are also called cold-cure resin varnishes. They are seldom used alone because the films are usually too brittle and lack desired adhesion.

Oleoresinous varnishes contain the following four main raw materials:

- a) Resins
 1. Natural, or fossil, gums.
 2. Synthetic esters, phenolics, or modified phenolics.



John M. Hafeli

- b) Oils
 1. Drying and semi-drying vegetable and fish oils.
 2. Non-drying oils chemically converted to drying oils.
- c) Driers
- d) Thinners, or solvents

Each of these constituents has a particular function to perform, thereby imparting a specific characteristic to the formulated varnish:

- a) The resins impart hardness, toughness, adhesion, gloss, waterproofness, ductility, and accelerated drying characteristics.
- b) The oils contribute to flexibility, toughness, adhesion, durability and relative waterproofness.
- c) The driers speed the rate of drying, particularly when higher quantities of oil are used.
- d) The thinners reduce viscosity, assist penetration, and act as carriers of the film forming portion to permit easy application and assist in the deposition of smooth, uniform films.

There are a number of commercially available ingredients to select in each of the four groups named, and this is most easily and completely exemplified by the following chart:

INGREDIENTS OF OLEORESINOUS VARNISHES

Oils	Resins	Driers	Thinners
Linseed	Rosin	Lead	Turpentine
Tung	Natural	Manganese	Normal Solvency Petroleum Thinners
Perilla	Ester Gum	Cobalt	Benzine VM&P Naphtha
Soybean	Phenolic (100%)	Zinc	Kerosene Mineral Spirits
Fish	Modified Phenolic	Driers are used in the form of Resinates	
Oiticica	Alkyd		High Solvency Petroleum Thinners
Dehydrated Castor	Coumarone- indene	Linoleates Naphthenates	Coal Tar Solvents Higher Alcohols
Bodied Oils		Octyl-oxy-acetates	

Limited as it is, this chart still reveals the great number of possibilities which are available to the formulator when he is making a choice of raw materials. Experienced formulators, having tested specific resins, oils, driers, and solvents in numerous studies in the past, select those ingredients which they know to be the best for the purpose and avoid those which are deficient in one respect or another.

The two most important materials to consider in every varnish are the resin and the oil. Because they both contribute so much to the ultimate varnish they are usually selected together and used together, one representing the chief reason for the selection of the other in many cases.

Resins, as used in varnishes, are divided into two main types, natural and synthetic. The natural resins include rosin, dammar, kauri, copal, congo, east india, and amber. These were the original resins used in varnish manufacturing procedures, and many of them have been supplanted by newer synthetic developments. Since many of them are being imported from overseas, particularly the Asiatic countries, they are becoming less and less practical from an economical standpoint.

The first synthetic resin of practical importance to the industry was ester gum, a glycerine esterified rosin introduced around 1900. Still a big factor in the varnish industry, ester gum has been superseded in many instances by modified phenolics, which contributed greatly to improved outside durability, toughness, gloss retention, and general chemical resistance. Introduced during the era when tung oil-ester gum varnishes were most predominant, they opened a new field of faster drying, more resistant, and cheaper protective coatings. They are made by modifying phenol-formaldehyde condensation products with rosins, rosin esters, or natural gums to make them soluble in vegetable oils. Combined with tung oil they were the basis for the first four-hour, or quick-drying, varnishes.

The 100% oil-soluble pure phenolic resins appeared around 1928-1930, and their acceptance in the industry has been rapid. They contribute exceptionally good water resistance and alkali resistance characteristics to varnishes and are used in the better spar varnishes marketed today. The pure phenolic resins are usually divided into two classifications, oil reactive and non-reactive. These two types are quite distinctive and must be handled in entirely different kettle procedures. The oil reactive resins eliminate water during the cooking reaction, and considerable foaming results when the vaporized water is forced from the resin-oil mixture. There are types in this group which foam greatly at two separate stages of the varnish cook, and it is usually necessary to hold the cook at a definite temperature for a period of time, or "split" the cook into separate phases, in order to keep the batch under control. Non-reactive phenolic resins do not foam excessively, and only normal precautions against over-bodilying and excessive viscosity are necessary.

The second of the most important components in a varnish is the oil. There are two main divisions of oils which are applicable, drying oils and semi-drying oils, and those non-drying oils which can be converted to drying oils. Drying oils include vegetable oils, chemically treated fish oils, and a few synthetic oils while semi-drying oils contain vegetable and fish oils only.

THE most important drying oil is linseed oil and its use, measured by weight or volume, exceeds all other oils combined. Originally linseed oil was used extensively in the raw form. Many of the earliest linseed oil varnish cooks made contained this raw product, and some of the undesirable properties caused by the saturated insoluble particles made it necessary to seek improvements. As a result, the first refinement, removal of the "break," was soon instituted. Other treatments were studied and more improvements obtained so that we now have various refined and semi-refined raw linseed oils available for varnish making. These include improved raw, non-break, alkali-refined, acid-refined, and varnish oil. In addition, there are a number of boiled oils, oxidized or blown oils, and bodied oils.

Many of those present today are familiar with the many variations of these oils which can be, or are, available for use today. Some of you represent oil producing concerns and can name the oils in general use by their specific trade names and give an accurate outline of their characteristics. In fact, there

are among you those who possess greater knowledge of oils and are therefore much better qualified to express themselves on oil technology than yours truly. For the benefit of future readers however, we believe a brief review of the types mentioned is in order.

Improved raw linseed oil does not "break" at any temperature, has a medium acid number of 4 to 6, and is used primarily in driers and those grinding and finishing varnishes where economic considerations predominate. Resultant varnishes are always quite dark and their use is consequently greatly limited.

Non-break linseed oil is essentially the same as improved raw oil, but it possesses a lower acid number of 2 to 4. Generally speaking, it is a little less reactive in those formulations and cooks which are more critical and more difficult to control.

Alkali-refined linseed oil is the most widely used type of linseed oil used in varnish production today. It is practically neutral (acid value usually less than 0.5) and therefore permits varnish cooks which are easily controlled and very stable. Formulators obtained the palest varnishes with this oil and vehicles for making white and pastel colored enamels were possible. Coupled with light-colored modified phenolic resins, this type of oil was used in enormous quantities to manufacture a white enamel vehicle for interior woodwork painting until supplanted, to a degree, by alkyd resin vehicles. Many high-grade enamels are still marketed with this oleoresinous type of vehicle, but relatively non-yellowing alkyds continue to displace them each year.

Varnish linseed oil is an alkali-refined oil of higher acid number in the range of 2 to 3. Acid-refined linseed oil has only limited use in those applications where reactivity is a major factor. Oxidized or blown oils are made by removing the "break" by passing air throughout the oil and holding it at a definite temperature for an extended length of time. When used in varnishes, they "body" or increase in viscosity rather rapidly and discolor considerably. They are sometimes incompatible with many of the high melt resins and, when judged to be practical in those cases, it is necessary to provide for rapid cooling and quick reduction to assure a successful batch.

Boiled linseed oil, as it is made today, contains soluble driers which have been added to alkali refined linseed oil at temperatures around 550°F. The resultant oil is very pale and is used primarily as an extender for house paints and other oil paints. Only limited quantities are used in varnishes.

Bodied linseed oil is obtained by heating alkali refined oil to a definite temperature and maintaining that temperature for a pre-determined period of time to establish a higher viscosity. They usually dry more quickly, are tougher, and have better water, alkali, and chemical resistance. Because they have been partially polymerized before they are used in varnishes, bodied oils are valuable raw materials to use in efforts to reduce bodilyng or cooking times. Very often they are used to chill or check varnish cooks. When used in varnishes employing high melt point, less soluble resins, it is necessary to exercise some caution when employing high viscosity oils because the oils are progressively less soluble as the viscosity increases.

The second drying oil to consider is tung oil, or china wood oil. This oil is outstanding in its basic

properties, and no other oil can offer quicker drying, faster bodying, more water resistant, more alkali resistant characteristics in varnishes. Limited in supply and often-times not sufficiently economical to warrant its general use, it is still partially employed in all varnish formulae of any consequence. Before the advent of modified phenolics the first improved varnishes were made of tung oil and ester gum. In fact, whenever the softer, lower melt point resins are used, it is almost compulsory to utilize tung oil to obtain maximum hardness and resistance characteristics. The original four-hour enamels, as we pointed out previously, were made with tung oil vehicles. Treated tung oils have been the main ingredient in several well-known patented finishes for many years. If foreign and domestic supplies of this oil were more plentiful and it were more economical to use, tung oil could be employed to a much greater extent than it is today.

Perilla oil, never used as raw oil, is bodied before it is employed in varnishes. It bodies more rapidly than linseed oil and consequently dries faster in all comparable formulations. Usually it is used in combination with other oils to give composite properties to the varnish.

Oiticica oil has gained some prominence as a replacement for tung oil in those varnishes where similar characteristics are desired at lower cost. Physically, this oil dries a little slower than tung oil, but it is faster than linseed or perilla oils and bodies, or increases viscosity more rapidly in cooking schedules. In typical modified phenolic or ester gum-varnish cooks oiticica oil bodies as rapidly as tung oil up to the point of gelation. Then tung oil increases viscosity more rapidly, effecting a production saving by shortening the bodying time. Many tests have been conducted which show that oiticica oil gives sufficient outdoor exposure results in phenolic varnishes to warrant substitution for all of the tung oil which was previously used.

Fish oil must first be treated for the removal of the highly saturated fatty acids before it can be considered a drying oil. Great strides have been made along the path of chemically processing fish oils, and more of the treated fish oils are being accepted each year. One of the outstanding disadvantages of any form of fish oil has been the characteristic odor which is inherent in this oil. Fortunately, this odor has been the object of determined study by the oil companies, and we are now entering into an era when odorless fish oils for use in varnish are a distinct factor. Already the air-drying oils are being used successfully, and we can reasonably expect varnish oil improvement to be satisfactory also.

THE outstanding development of the oil industry, as far as general varnish cooking is concerned, has been the production and utilization of dehydrated castor oil. By the refinements which are now used this previously non-drying, non-usable oil can be converted into a useful, highly desirable fatty acid for a wide range of varnishes. Originally it was considered a good partial substitute for tung oil, and its economic value was first emphasized in this direction. However tests have shown that it can take its place as a distinct varnish ingredient and, as such, it is a major factor in the production of long and short oil

varnishes where hardness, flexibility, and durability are desired. True, it does not equal tung oil in all features, but it has produced better results than many of the other drying and non-drying oils used for specific applications. Some formulators prefer it to linseed oil in instances where color is of major concern. Dehydrated castor oil is used in several viscosity ranges and serves as a chill or check on many tung oil cooks with low solubility resins.

Recently, because the oil is plentiful and the domestic market is able to supply it in acceptable forms, the use of soybean oil has increased steadily. This is a semi-drying oil in character and is usually used in conjunction with harder oils like tung oil, oiticica oil, dehydrated castor oil, and linseed oil. Soybean oil can be "bodied" in much the same manner as linseed oil and, as a result, it is used at Q, U-V, or Z₁-Z₂ viscosity to suit the specific need. Very few varnishes contain soybean oil alone because the films are too soft, fail to give sufficient resistance to water, alkali, and weather and lose gloss too rapidly. Primarily, all types of soybean oil are most useful as "checking" oils for cooks made with the harder types.

Before discussing any specific varnish cooks and thereby pointing out individual characteristics, it will be in order to describe the general meaning of the term "oil length." The "oil length" is the number of gallons of oil used for every 100 pounds of resin employed. When we say that a varnish is 25 gallons long, or 12 gallons long, we mean that the solid or non-volatile portion of that varnish contains 25 gallons or 12 gallons of oil for every 100 pounds of resin used. Descriptively, spar varnishes, because they contain a high amount of oil, are known as "long oil" varnishes while rubbing varnishes, containing low amounts of oils, are described as "short oil" varnishes. This convenient method of describing a varnish was established years ago, and it still represents the most understandable description of varnish formulations today although expressions in percentage figures are becoming more popular as full understandings of the complex reactions become known.

With this basic background of the various types of oils and resins used in varnish production, a further study of the specific uses of varnishes can be made. Describing the specific oils which are used in each case.

WE have all heard of spar varnishes at one time or another, and they are of prime concern when new oil materials are introduced to the industry. This is understandable when we consider that they are usually 35 to 50 gallons long or contain 72-80% oil in the solid, film-forming portion. If an oil passes the rigid water resistance, gloss retention, salt spray resistance, and general outside exposure tests of a spar varnish, it definitely has something to offer to the varnish formulator. Spar varnishes require these highly desirable characteristics, and the better types of oil are necessary to obtain them. That is why tung oil, oiticica oil and, more recently, dehydrated castor oil give the best results even when the older type ester resins are used. Today tung oil is cooked with pure phenolics, of the para phenyl phenol or alkyl phenol type, to produce the most desirable results. Compromise products are available which con-

tain percentages of modified phenolic resins (usually medium to high melt) or percentages of softer oils. This is usually done for economical reasons or to provide products which do not have to withstand the more rigid tests. A typical spar varnish cook, using a pure phenolic resin, is given below:

Spar Varnish		lbs.
Pure Phenolic Resin.....		94.50
Tung Oil		227.00
Bodied Linseed Oil (Z ₂).....		37.75
Mineral Spirits		359.00
6% Cobalt Naphthenate.....		1.50
6% Manganese Naphthenate.....		0.75
24% Lead Naphthenate.....		2.75

Heat the tung oil to 350° F. Add the pure phenolic resin slowly and hold at 350° F. for 5 minutes until reaction is over. Heat to 450° F. and hold 5 minutes for foaming to subside. Then go to 525° F. and hold 8-10 minutes. Chill with Z₂ linseed oil. Cool to 400° F., thin, and add driers.

This particular varnish will dry overnight to a hard film which will withstand 24 hours' immersion in water, 200-300 hours' salt spray resistance, and have sufficient flexibility to withstand exposure in salt water atmospheres for over a year without appreciable visual failure.

Spar varnishes are frequently used as vehicles for aluminum paint, especially when the application is intended to withstand water exposures. As a matter of fact, there is a Navy Department specification which is designed to give the most resistant coating for above water and under water use. This is Navy Department Specification 52-V-15, employing a 25-gallon para phenyl phenol pure phenolic resin and 50% alkali refined oil—50% tung oil. This vehicle, like all other phenolic type varnishes, is not particularly suited for a ready-mixed aluminum paint but is usually supplied in a double-compartment container. The aluminum and the varnish are then mixed at the point of application. The formula is described as follows:

52-V-15c Varnish, Mixing (for Aluminum Paint)

	lbs.
Para Phenyl Phenol Resin.....	121.00
Alkali Refined Linseed Oil.....	119.00
Tung Oil	119.00
Mineral Spirits	297.00
Xylol	73.00
6% Cobalt Naphthenate.....	1.94
6% Manganese Naphthenate.....	.85
5% Calcium Naphthenate.....	2.43

Take half of the resin and the linseed oil to 560° F. Hold for one hour and add the remaining resin slowly, holding the temperature at 560° F. and making sure each addition is clear before adding further increments. Add the tung oil slowly and reheat to 465° F. Hold for viscosity (approximately 20-40 minutes). Reduce with solvents and add driers.

Aluminum paints, generally speaking, require a neutral, or near neutral, vehicle to be stable. Consequently, neutral oils, such as alkali refined, and neutral resins are employed in most cases. Some of the most satisfactory aluminum paints are made with 100% neutral oil as the vehicle. Coumarone-indene resins have the unique faculty of permitting aluminum flakes or powders to leaf easily and uniformly, and they are used frequently in cold-cut spirit varnishes. They can also be cooked into highly satisfactory varnishes, thereby producing a vehicle with

better flexibility and durability. Most aluminum paint varnishes are 12½-25 gallons long, although some longer oil marine types are favored for maritime exposures.

UTILITY, or general purpose, varnishes comprise a major percentage of the trade sales varnish distribution in this country today. These varnishes are not usually designed for any specific purpose, and the dealer or distributor can easily recommend them for any use around the home. Utility varnishes have therefore been used to reduce house paints, extend floor enamels, finish woodwork and furniture, and refinish house articles ranging from toys to dining room sets. As a result these varnishes are designed to dry at a medium rate, reach hardness overnight, and be compatible with oils, other varnishes, and long oil alkyds. They are formulated to have fair to good water and alkali resistance, and they must be priced in a range which is attractive to the average household user. The resins are ester gum, or ester gum-modified phenolic blends, and the oils are usually blends of 25% tung oil, 75% linseed oil or soybean oil, or mixtures of dehydrated castor oil and linseed oil and/or soybean oil. They are formulated to be 18-25 gallons long, affording some flexibility and toughness to the film. Bodied oils are used frequently to obtain higher viscosities and improve the general rate of drying. A typical utility, or general purpose, varnish cook is shown below:

Utility, or General Purpose Varnish

	lbs.
Modified Phenolic Resin.....	125.00
Tung Oil	150.00
Bodied Linseed Oil (Q).....	50.00
Bodied Linseed Oil (Z ₂).....	50.00
Mineral Spirits	375.00
6% Cobalt Naphthenate.....	2.00
24% Lead Naphthenate.....	5.00

Take resin, tung oil, and Q bodied linseed oil to 550° F. in 36 minutes. Hold for 15 minutes and chill with Z₂ bodied linseed oil. Cool to 425° F. and reduce with mineral spirits. Add driers.

Before the days of alkyds and the so-called non-yellowing enamels of recent years, formulators were forced to make interior enamels with varnish vehicles. The yellowing problem, created primarily by the color change in the oil, was a constant cause for study and chemists sought improvements by changing oils and resins frequently. Before major oil refinements were introduced, they tried to use maleic ester gums in tung oil and linseed oil varnishes, but their stability was limited and they lacked the necessary resistance to washing and cleaning. The best balance of all properties desired was found in a 20- to 25-gallon long butyl phenol modified-phenolic resin cook made with alkali refined linseed oil and a small percentage of tung oil. When the economics of the oil market permitted the move, tung oil was used alone or it was modified with only a small amount of linseed oil to check the cook. The introduction of dehydrated castor oil improved the color to a degree, at some sacrifice to other factors, and today this oil is used prominently in interior enamel vehicles. It might be added that penta ester gums have gained preference over glycerine ester gums also, permitting higher viscosities, better color, and better color retention. In many instances formulators have de-

signed varnishes by blending ester gum and pure phenolics in the cooking procedure, thereby creating their own modified phenolic resin. A typical enamel vehicle varnish, and it is only one of many types used, is outlined below:

White Enamel Varnish

	lbs.
Penta Ester Gum Resin.....	106.25
Dehydrated Castor Oil (U-V).....	85.00
Dehydrated Castor Oil (Z ₂).....	85.00
Tung Oil	85.00
Mineral Spirits	361.00
6% Cobalt Naphthenate.....	1.75
6% Manganese Naphthenate.....	0.75
24% Lead Naphthenate.....	2.50

Take resin, tung oil, and U-V castor oil to 550°F. in 36 minutes and hold 8 minutes. Chill with Z₂ castor oil. Cool to 400°F. and thin. When cool, add driers.

We speak of spar varnishes being in a class by themselves because they serve a definite, rigidly outlined application. In this same category of special-purpose vehicles we should also include those varnishes which are designed for making attractive, long-wearing floor enamels and porch and deck enamels. These vehicles must be resistant to abrasion and resistant to frequent washings and scrubbing with water containing soap and detergents. They must dry reasonably fast to give enamels of high gloss and gloss retention. Those intended for outside use must likewise be durable under all weather conditions and allow only minimum chalking under this exposure. Most concerns would like to make, or use, one varnish to serve both interior and exterior purposes, but the cost of exterior types is usually somewhat higher and there is no need for such expensive vehicles for inside enamel work. Porch and deck enamel varnishes contain higher percentages of phenolic resin and more of the costlier tung oil and/or dehydrated castor oil. Selection of the oil is governed by the resin to be used because higher viscosity oils have a tendency to be less compatible with high melt point resins usually used in this type of varnish. A typical porch and deck enamel varnish is outlined as:

Porch and Deck Enamel Varnish

	lbs.
Pure Phenolic Resin.....	119.00
Alkali Refined Linseed Oil.....	238.50
Mineral Spirits	358.00
6% Cobalt Naphthenate.....	1.50
6% Manganese Naphthenate.....	1.00
24% Lead Naphthenate.....	5.00

Take oil and resin to 575°F. for 1½ hours. Cool to 450°F. and thin with mineral spirits. Add driers.

When interior floor enamel varnishes are considered, there is less desire for the exterior durability qualities required in the porch and deck types. As a result, the resins are of lower value, usually combinations of ester gum and/or modified phenolics, and smaller quantities of the more durable oils are employed. Linseed oil is a popular ingredient in these vehicles and percentages of tung oil and/or oiticica oil are included to improve scuff resistance, toughness, and water and alkali resistance. Where good durability is desired, formulators employ a modified phenolic resin and use all linseed oil. This type of vehicle has the benefit of the highly desirable phen-

olic resin properties and allows the use of an oil which is generally more reasonable than tung oil. A varnish of this type is as follows:

Floor Enamel Varnish

	lbs.
Modified Phenolic Resin.....	121.00
Alkali-Refined Linseed Oil.....	242.00
Mineral Spirits	358.00
6% Cobalt Naphthenate.....	2.01
24% Lead Naphthenate.....	3.02

Take the oil and resin up to 575-580°F. in approximately 40 minutes. Hold at this temperature for 2½-3 hours, pull from the fire, cool to 450°F., and thin with mineral spirits. Add driers.

Just as a floor enamel vehicle requires certain properties, so also must a floor varnish produce a film which will be tough, hard, scuff resistant, and able to withstand cleaning and washing. A standard varnish for the purpose is outlined as:

Floor Varnish

	lbs.
Modified Phenolic Resin.....	121.00
Bodied Linseed Oil (Z ₂).....	194.00
Tung Oil	48.50
Mineral Spirits	363.25
6% Cobalt Naphthenate.....	2.00
6% Manganese Naphthenate.....	1.50
24% Lead Naphthenate.....	2.50

Take resin and oils to 550°F. in 36 minutes and hold 16 minutes. Cool to 400°F. and add mineral spirits and driers.

Gymnasium floor varnishes, and those used on roller rink floors and other similar large areas, demand more scuff resistance and must withstand stronger cleaning compounds so a better grade of finish is necessary, as:

Gymnasium Floor Varnish

	lbs.
Modified Phenolic Resin.....	186.00
Pure Phenolic Resin.....	91.75
Tung Oil	444.00
Bodied Linseed Oil (Y).....	111.00
Mineral Spirits	832.75
6% Cobalt Naphthenate.....	4.52
6% Manganese Naphthenate.....	3.42
24% Lead Naphthenate.....	5.72

Heat resin and tung oil to 525°F. in 30 minutes. Hold for viscosity and check with linseed oil. Cool and thin to 50% non-volatile with mineral spirits.

Finishing furniture is a specific art, and those who are employed in the reliable manufacturing plants can vouch for the control which is exercised to assure uniform, smooth finishes. Furniture varnishes demand special formulating attention because they must preserve beauty as well as provide protection. As a result raw materials must be selected to prevent early and excessive checking or gloss failure and still be hard enough to be rubbed to a satin or semi-gloss sheen. All furniture varnishes are therefore necessarily short, ranging from 12-18 gallons in oil length. Usually the phenolic, or modified phenolic, resin used is one of high melt point and high phenol content to contribute necessary hardness. High melt point maleic ester gum varnishes are also used. Since they are less soluble in oils like tung oil and dehydrated castor oil, it becomes necessary to use blends of oils to get clear finishes. This consideration also permits greater flexibility to withstand the cold check

cycle test conducted on furniture finishes. A typical formula is shown below:

Furniture Varnish

	lbs.
Modified Phenolic Resin.....	156.00
Tung Oil	164.00
Bodied Linseed Oil (Z).....	46.75
Mineral Spirits	374.00
6% Cobalt Naphthenate.....	1.25
24% Lead Naphthenate.....	3.10

Take the resin and tung oil to 565°F. in 37 minutes. Hold 10 minutes and add the linseed oil. Let temperature drop to 500°F. and held for 10 minutes. Pull from fire, cool to 450°F., thin with mineral spirits, and add driers.

Because they have had specific importance in many cases we should include alcohol resistant varnishes as part of the discussion on furniture varnishes. These finishes, as their name implies, must withstand alcohol without softening the film or causing it to discolor. They are usually 100% tung oil varnishes, and a resin is selected to enhance the resistance desired.

	lbs.
Pure Alkyl Phenolic Resin.....	107.00
Tung Oil	253.00
Mineral Spirits	360.00
6% Cobalt Naphthenate.....	2.11
6% Manganese Naphthenate.....	.42
24% Lead Naphthenate.....	5.27

Take the oil and resin to 565°F. in approximately 37 minutes and hold at this temperature for 10 minutes. Water cool to 450°F. and reduce to 50% non-volatile with mineral spirits. Add driers.

In many instances this type of varnish can also be used as a highly satisfactory acid resistant varnish. Usually they are at least 30 gallons long.

The enamel formulator has at his command a great number of varnish and other type vehicles from which he can select those which have performance characteristics he desires. Blends of several types are often necessary, and we want to mention the important blending varnishes which have served, and will continue to serve, their purpose many times. They are known as "hardening" or "leveling" varnishes. Basically they are short (8-15 gallons long), high melt point modified phenolic-tung oil varnishes, reduced with all coal tar solvents or a blend of coal tar and aliphatic solvents. They are intended to be miscible in most all other types of enamel vehicle varnishes and have been used to great advantage when blended with alkyds as well. Hardness, toughness, gloss, increased water and alkali resistance, and resistance to water spotting are achieved when they are properly used. They have been employed in automotive finishes, toy enamels, floor enamels, wall primers and sealers, trim paints, and in fact wherever the above mentioned properties are to be improved. A valuable tool for any chemist, they are typically represented by:

Hardening and Leveling Varnish

	lbs.
Modified Phenolic Resin.....	168.00
Tung Oil	210.00
Mineral Spirits	308.00
Turpentine	62.00
6% Cobalt Naphthenate.....	1.75
24% Lead Naphthenate.....	4.25

Take resin and tung oil to 500°F. and hold approximately 10 minutes. Cool to 425°F. and reduce with blend of solvents. Add driers.

The automotive industry, determined to make itself the most quality-minded finishing enterprise, has always maintained a set of finishing specifications designed to force vendors to give them the better grades of materials. For years they used varnish type dipping primers wherever possible, demanding dip tank stability, along with hardness, enamel and lacquer hold-out, salt spray and water resistance, and easy sanding characteristics. These primers always contained tung oil for maximum quality, but when it was economically wise to use lower priced oils, percentages of linseed oil and dehydrated castor oil were substituted. In some instances synthetic alkyd vehicles have been incorporated in primers and primer surfaces to accommodate baking cycles, but the varnish type is still in use in many plants.

Dipping Primer Varnish

	lbs.
Pure Phenolic Resin.....	116.00
Run Congo	20.00
Dehydrated Castor Oil (Z ₂).....	94.00
Raw Linseed Oil.....	48.00
Tung Oil	94.00
Mineral Spirits	372.00

Take resins and dehydrated castor oil to 580°F. in approximately 37 minutes. Hold for 27 minutes and check with raw linseed oil and tung oil. Cool to 425°F. and reduce with mineral spirits. (Driers are added to the finished primer.)

No varnish discussion would be complete without including remarks about the use of tung oil in baking wrinkle enamels. These industrial finishes are obtained when enamels containing bodied tung oil and/or tung oil varnishes are formulated in such a manner that the top surfaces are permitted to oxidize faster than the lower layers of the film. Subsequent baking causes the surface to "draw" or "gather" into definite wrinkle patterns. These patterns can be controlled by pigmentations and drier additions to give a wide range of finishes to hide otherwise objectionable defects on castings and steel parts.

This ability to "wrinkle" has been characteristic of tung oil because the conjugated double bonds of the predominant eleostearic acid permit faster absorption of oxygen. The surface sets faster as a result. Oiticica oil and dehydrated castor oil possess this same general faculty to a lesser degree, but neither is as desirable as tung oil. Very often this ability to wrinkle is detrimental, especially when a smooth surface was anticipated. Many formulators know this representative wrinkle varnish:

Wrinkle Varnish

	lbs.
Modified Phenolic Resin	179.00
Tung Oil	282.00
Lead Acetate	7.25
Xylol	311.00

Run the resin and tung oil to 480°F. in approximately 30 minutes. Add the lead acetate slowly, and after this is taken up (when head subsides), raise the temperature to 500°F. Hold at 500-510°F. for 10-15 minutes and cut to 60% N. V. with xylol.

Another phenomenon can be achieved in tung oil varnish films by exposing wet films to an atmosphere of nitrous oxide and other vapor formations caused by the combustion of natural or manufactured gas in ovens in which circulation is impeded. Coatings described as "crystal" finishes are produced in which

a unique crazed effect is predominant. It might be well to point out here that the most objectionable feature of tung oil in baking and in air-drying applications is its tendency to gas check. This tendency, which causes the dried films to display a frost or very pronounced "checking," is usually encountered in longer oil varnishes but is occasionally noticed in short varnishes as well. Proper selection of resins, chiefly phenolic types, can minimize the "gas checking" tendency in the short 10- to 18-gallon varnishes. These resins will permit the oil to be held at a high temperature until the oil has polymerized sufficiently. It is necessary to attain 550°F. at least 5-8 minutes to "gasproof" a varnish in most cases. Corresponding lower temperatures and longer hold periods will produce equally good results.

Other resins, such as high melt point phenolic resins and ester gums, will not always effectively combine with the oil to obtain "gasproofness." It is often necessary to modify these resins with percentages of a pure phenolic resin to obtain good results. Another procedure involves modification of the tung oil content with portions of other oils, such as linseed oil and dehydrated castor oil. Greater modifications are needed as the oil strength is increased, i.e., 10- to 20-gallon lengths require approximately 30% modifications and 25- to 40-gallon lengths demand as high as 40% modification, depending on the resin employed. Modifications with refined or bodied oils can likewise be utilized, each providing effective "gasproofness" with specific resins.

Because the degree of gasproofness of a varnish is directly related to drying speed, manufacturers are very conscious of this characteristic in all finished products. This is especially true in varnishes which

are 25 gallons long or longer. It has been found that oil which has been gasproofed will dry more slowly than oil which still gas checks. The ultimate film hardness is about equal. There is a critical point therefore in every tung oil cooking procedure beyond which the varnish will exhibit slower drying as a sacrifice to gasproofness. There is also the danger of permitting too much polymerization of the oil in an attempt to insure gasproofness. Gel formations and reactivity with pigments result from excessive polymerization. Each cook therefore becomes a problem in itself and, by careful selection of resins and control of heating rates, successful varnishes can be made.

The scope of this discussion has been very general, and there are probably those who wish that it had been more specific and detailed. By choice and, we believe by necessity, it was deliberately intended not to be too concrete and precise. The chemical reactions which take place when a varnish is cooked are complicated, and the explanations for these reactions are lengthy and technical. The number of oils available and the various grades and refinements of those oils make the overall varnish cooking procedure still more complicated and involved. We appreciate that the various oil refining companies have done wonders in the development and marketing of new products. It would have been impractical to discuss all of them in specific cooks and show how they differed from types previously used. Comparisons of a few oils in similar varnish cooks would have produced some data, but it would not have been complete and therefore inconclusive and probably misleading. We have tried therefore to bring to your attention the types of varnishes most predominantly used and the oils employed therein.