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Part II

Tung Oil

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TUNG OIL, or Chinese wood oil, was used in China and Japan for many centuries for water-proofing wood, paper, and fabrics; and at a very early period both the Chinese and Japanese discovered how to treat the oil so that, upon drying, it would give a clear hard film.

In China the oil was obtained from a specific tree with the species name of *Aleurites Fordii* from central and western parts. In southwestern China the species that grew best was the *Aleurites Montana*. There are many botanical differences between the two trees, but from the standpoint of the user of tung oil the difference lies in the gelling time of the two oils. The *Montana* variety is somewhat slower. In China the two oils were usually mixed before shipping. No harm was done since both oils made excellent end-products in spite of the different gel times.

From about 1923 tung tree planting on a commercial scale has been in progress in the United States. In the beginning this was confined to Florida, but now it is spread over parts of Florida, Georgia, Alabama, Mississippi, Louisiana, and Texas. Probably the largest individual plantings are in Mississippi, Florida, and Louisiana. An acid soil, plenty of rainfall, and good root drainage are needed; an area about 50 miles wide and just north of the Gulf of Mexico seems to satisfy these conditions.

The production of the oil from the fruit is usually done by breaking the outer hull of the fruit, removing and then pressing the seeds. The oil content of the seeds ranges from 50–60%, and based on the whole fruit this analysis is 18–22%. The pressing of the oil in China was on a primitive basis. The fruit was allowed to ferment so that the hulls would be easily

cracked open to get at the seeds. The seeds were roasted in iron pots and then pressed in crude presses that derived their force from driven wedges. In the United States the fruit is first freed of dirt, sand, and branches, then sent to hulling machines that remove the outer covering of the seeds. The seeds are dried and then pressed in expellers. The crude oil is filtered and stored for marketing. No further refining is necessary.

The high reactivity of tung oil is explained somewhat by its fatty acid composition. It has a very high concentration of a triply conjugated bond acid called eleostearic acid. The total fatty acid composition is about 79.5% eleostearic acid, 15.0% oleic acid, and 5.5% saturated acid.

These figures change somewhat from year to year, depending on the quality of the crop of fruit. Eleostearic acid is described as: *cis, trans, trans* 9,11,13-octadecatrienoic acid. It is primarily the reactivity of this conjugated system that gives us the gellation test for tung oil.

When the oil is heated above 536°F., it has the unique property of solidifying to a jelly-like mass in 9 to 12 min. This test, the Browne heat test, has become a measure of the quality of the oil.

It is this fast rise of viscosity to the gel state that permits rapid production of varnishes. The gel time of 9–12 min. is characteristic of the oil derived from the *Aleurites Fordii* variety of tree contrasting with longer gel times and correspondingly lower eleostearic contents from the *Montana* variety of oil.

The presence of conjugated systems in the eleostearic acid permits *cis-trans* isomerism, so we find eleostearic acid existing in two forms: the *alpha* variety

or the *cis, trans, trans* and the *beta* form or the *trans, trans, trans*. The *alpha* acid melts at 118°F., and the *beta* acid at 160°F. This is remarkable for an unsaturated acid if we remember that the saturated stearic acid melts at 156°F. When we consider the oils, *alpha* oil (oil containing mostly *alpha* acid) is reported to melt at −45°F. and *beta* oil is solid at room temperature. The conversion of *alpha* oil to *beta* is accomplished by means of various catalysts, *e.g.*, iodine, potassium iodide, sulfur, and strong acids. Ultraviolet light will also promote the isomerization. The *beta* form of the oil is the most stable, and *alpha* oil will tend to convert slowly but will take several years without catalysts. When tung oil is heated, it will increase in viscosity; this probably happens by means of the diene reaction between neighboring fatty acids. The diene reaction can take place either in *cis* or *trans* systems (at different rates, of course), therefore varnishes prepared from either *beta* or *alpha* oil are indistinguishable after cooking. In general, alkyds and varnishes can use either oil and get the same end-results. In polymerization and pure diene reactions it is advisable to use the beta oil.

All commercial tung oil contains *alpha* and *beta* acids, but *beta* oil contains sufficient *beta* acid (approximately 10–15%) to make the oil solid at room temperature. The A.S.T.M. specification recognizes that some pure tung oil may be solid by stating that the appearance of the sample under test should be clear and transparent at 149°F. At this temperature all *beta* oil will be liquid.

From early recorded history in the Orient tung oil has been used primarily for coatings even though frequently it was used as a fuel for light and heat. Prior to the use of tung oil by western countries, varnishes were made from linseed oil and natural resins. A fossil resin, such as Congo copal, was fused at 550°F. When the resin was thoroughly liquefied, linseed oil, raw or bodied, was added and the batch was reheated to 580°F. and held at that temperature until the proper viscosity was obtained. This process could possibly take 8 hrs., a little less if bodied oil were used. The varnish dried in about 12 hrs., and the resulting film was glossy but not hard or water-resistant. When the conversion to tung oil was made, varnish-makers had to revise radically their methods because tung oil bodied so rapidly. For example, a 20-gal. tung ester gum cook could only be held at 560°F. from 2 to 4 min. and then had to be chilled back with 5 gal. of bodied oil. Further external cooling was necessary before thinning. Instead of taking 8 hrs. to make a varnish, the new total time was about an hour. Furthermore the varnish dried in 6 hrs. and was very water- and alkali-resistant. As a result, one of the largest uses for tung oil was in the production of practically every type of industrial, trade sales, and marine varnish and paint.

Tung oil is used in some alkyd resins. Its inclusion in a formula will yield a resin of high viscosity and good water resistance. It is usually not put in formulae as the sole oil since gellation will occur because of the generally long reaction time of alkyds. However high concentrations of tung oil can be used if some rosin or other fatty acid is used in the reaction mass since it is well known that the gel time of tung oil is retarded in the presence of free acidity. One way of producing a 100% tung oil alkyd is to use tung fatty acid or tung methyl ester with a small

quantity, say, 1% of zinc resinate. The latter acts as an ester interchange catalyst and as a gel-retarding agent. However, as mentioned above, tung oil is usually used with soybean oil to increase the water resistance of the alkyd, or it is used with the long-oil tall oil alkyds, which suffer from a slight tack after drying. The tung oil snaps up this drying time.

During World War II tung oil was under allocation, and during the Korean conflict it was selling for as high as 40¢/lb. The unavailability of the oil and its unstable price during these conflicts discouraged users of the oil, consequently many substitutes were devised. The result was that tung oil lost quite a bit of the market it had. Today 45,000,000 lbs. are used yearly in varnishes and alkyds; varnishes take a larger portion. After World War II the United States used as much as 130,000,000 lbs. The Tung Research and Development League has attempted to regain some of the loss by developing new uses for tung oil, and a few developments will be mentioned.

Tung fatty acids and tung methyl esters were easily prepared, so we looked for ways of using these derivatives. Some of the compounds prepared were epoxy esters, polyesters, and polyamides. A very fast-drying epoxy ester can be made from 1 equivalent of epoxy resins (Shell 1001) (Araldite 6071), 0.2 equivalent of tall oil fatty acid, and 0.2 equivalent of tung oil acid. If maleic anhydride is adducted on tung acid, a tricarboxylic acid anhydride is formed. The anhydride ring can be broken by merely heating the product with an alcohol and forming an ester dicarboxylic acid compound. This latter compound can be reacted with di-amines to form polyamides which can cure epoxy resins.

We have successfully hydroxylated tung oil but only 1 of the 2.6 average double bonds per fatty acid molecule. It is a viscous liquid, unstable in air, and skinning over immediately upon exposure. We have blended this product with tolylene di-isocyanate and cured a film cast on steel. It had a Sward hardness of 80 yet was easily bent over a 1/8-in. mandrel. The film was unaffected after one month of immersion in a 5% alkali solution.

We have exposed tung oil to high-energy radiation in order to explore possible new reaction products that would be formed. When the oil was exposed to a 763,000 r/hr. Co-60 source for 24 hrs., it suffered a slight loss of refractive index, reduction of I.V., and a small conversion of *alpha* oil to *beta*. In seven days the oil gelled to a white powder. Next the oil was placed in a water-cooled hole in the Brookhaven neutron pile and exposed to a flux of 10^{12} neutrons/cc./sec. After 2 hrs. the oil was bleached almost white, and after 24 hrs. the oil was gelled. The oil which was exposed for 8 hrs. was mixed, cold, with

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ester gum. The mixture dried in the same time as a cooked varnish of the same composition. In another experiment the oil was exposed to a 1 MEV electron beam for increasing lengths of time. In general, the longer the exposure, the more *alpha* to *beta* conversion; in the longer exposures we found the almost complete disappearance of eleostearic acid. We had to assume the oil was polymerized. Again the polymerized oil was very light in color and made a fast-drying vehicle by merely mixing the oil with an ester gum-mineral spirit solution.

A MORE detailed discussion will be given of our latest development, one which is most promising for the increased use of tung oil. This is the increased adhesion for chalked surfaces, caused by the addition of tung oil to emulsified polymers. As is well known, it is difficult to make exterior paints from PVA, acrylic, and butadiene styrene latices mainly because of their poor adhesion to powdered surfaces. It has been the practice to use oil primers on such exterior surfaces; but now by the mere addition of raw tung oil containing a wetting agent we can overcome poor adhesion of the polymers. We have a three-year exposure of house paint containing 15% tung oil based on vehicle solids (remaining vehicle is polyvinyl acetate). The previous coating on the house was well chalked, but after three years there are no visible signs of cracks, breaks, or flaking.

A study by laboratory methods showed an increase of adhesion in tung-polymer paints. Table I indicates the composition of a conventional interior paint with and without tung oil.

The emulsifiable tung oil's composition is 92% raw tung oil and 8% nonionic wetting agent. The oil contained 0.03% Co and 0.4% Pb as naphthenate. The nonionic agent could be practically any commercial brand. We used Tergitol NPX.

TABLE I

	L-622	L-623
Water	365	400
Wetting agent[1]	6	6
Potassium tripoly phosphate[2]	1	1
Defoamer[3]	1	1
Ethylene glycol[4]	35	35
Butyl cellusolve acetate[5]	5	5
Titanium dioxide[6]	225	225
Calcium carbonate[7]	100	100
Silica[8]	50	50
Clay[9]	75	75
Thickener[10]	4.5	4.5
Polyvinyl acetate emulsion[11]	325	162
Emulsifiable raw tung oil	......	89

These two paints were intermixed to give nine paints with varying amounts of tung oil:

Paint	Tung oil on vehicle N.V.
	%
L-622	0
A	6.25
B	12.50
C	18.75
D	25.00
E	31.25
F	37.50
G	43.75
L-623	50.00

Films were applied and various aspects were studied.
[1] Advawet-33, Advance Solvents and Chemical Corporation, New Brunswick, N. J.
[2] Potassium tripoly phosphate, Victor Chemical Works, Chicago, Ill.
[3] Foamicide 581B, Colloids of Carolina Inc., Newark, N. J.
[4] Ethylene glycol, Union Carbide Chemical Company, Atlanta, Ga.
[5] Butyl cellusolve acetate, Union Carbide Chemical Company
[6] Titanium dioxide, E. I. du Pont de Nemours 'and Company
[7] Snowflake Whiting, Thompson, Weinman and Company
[8] Goldbond R, Tamms Industries Inc.
[9] Iceberg Clay, Burgess Pigment Company, Sandersville, Ga.
[10] Cellosize WP-4400, Union Carbide Chemical Company
[11] Resyn 12K55, National Starch Products Company

Figure 1 indicates the effect of tung oil on the hardness of PVA paints. Films of paints L-622, L-623, and each of the intermixes were cast on glass plates at 3 mil (.003 in.) wet film thickness, using a Bird applicator. These films were dried for 24 hrs. at 78°F. and 70% relatively humidity. Sward-hardness was measured on each film, and a curve (Figure 1) was plotted, relating hardness to tung oil content. Figure 1 shows that the addition of tung oil plasticizes the film with the greatest effect evident after the first additions. Further additions of tung oil however have only a slight additional plasticizing effect on the film. At the level of 50% tung oil and 50% PVA there is a hardness of 6.6% compared to a 16% hardness for 100% PVA resin.

Hardness measured on these films with pencils bear out the Sward-hardness data. These data show that tung oil definitely plasticizes the film of these emulsion paints.
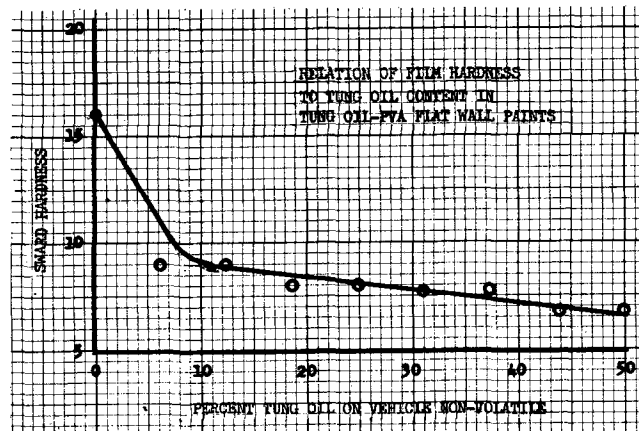

FIG. 1.

AS ADHESION is a difficult quantity to measure, a method was devised to evaluate adhesion by using a Reverse Impact Tester. Films of the paints were applied to aluminum "Q" panels by spraying. Panels were air-dried 2 hrs. then aged for 24 hrs. at 220° F. in an electric oven. Reverse impacts of 10, 20, 30, 40, and 50 inch-pounds were run and evaluated by the following ratings:

Description	Rating
No cracks or breaks in film	0
Very slight cracks	1
Slight cracking	2
Cracking	3
Cracking and separation of film	4
Severe cracking and flaking of paint	5

Readings were taken, and an Adhesion Factor was derived by a summation of the rating for the five impacts at increasing loadings; thus the lower the Adhesion Factor number, the better the adhesion of the film to the substrata. These data for each film were plotted against percentage of tung oil in the film (Figure 2). This shows that the best adhesion was obtained with high loadings of tung oil. The curve is almost a straight-line function. Therefore the dry adhesion of PVA-tung oil paints is improved as the quantity of tung oil is increased.
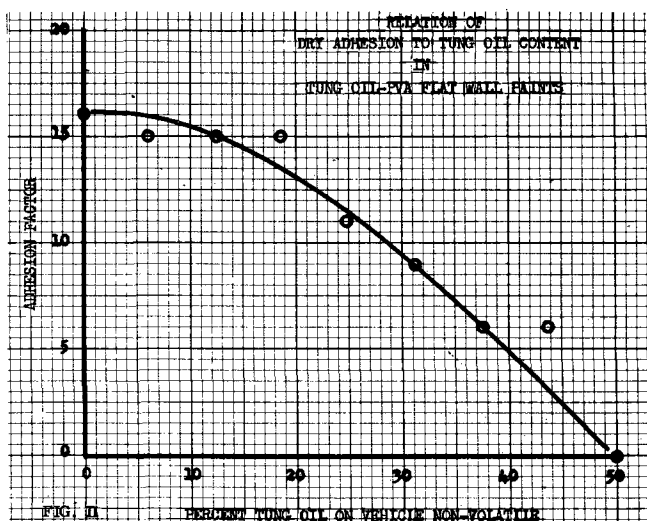
Fig. 2.

Effect of Tung Oil on Wet Adhesion

Paints were applied to aluminum "Q" panels by spraying, air-dried 2 hrs., then aged for 24 hrs. at 220°F. in an electric oven. The panels were cooled, then immersed in boiling water for 5 min., and reverse impacts were run immediately after removal from boiling water at 10, 20, 30, 40, 50, and 60 inch pounds. The indentions were read by the previously established rating scale, and their Adhesion Factor Numbers were determined. These data were plotted similarly against the percentage of tung oil in the films (Figure 3).
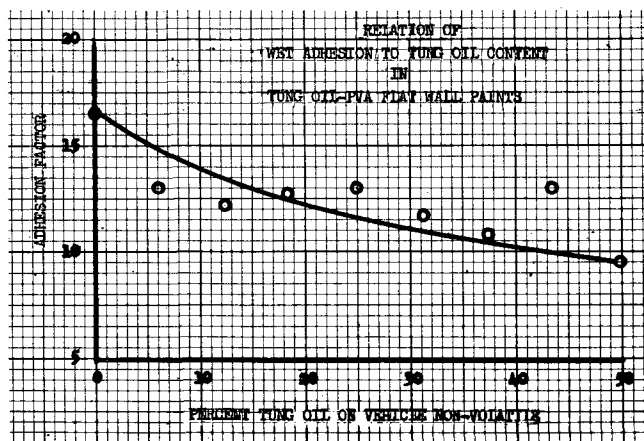

Fig. 3.

This curve shows that the wet adhesion of PVA-tung oil flat wall paints is greatly improved by increasing the amounts of tung oil.

These adhesion tests were done on aluminum, but the results correlate with work on test fences and houses in southern United States. The oldest coating on one house is three years old with no sign of adhesion failure.

In order to demonstrate the low degree of yellowing caused by the addition of tung oil, the following was devised. Films were applied to aluminum "Q" panels by spraying, air-dried 2 hrs., and then aged in an oven for 2 4hrs. at 220°F. After cooling, the color of each panel was measured with the Gardner Color Difference Meter. Yellow readings were plotted *versus* the amount of tung oil in the respective paints (Figure 4). The curve shows that small additions of tung oil increase yellowing to a very marked degree; a plateau is reached from 12.5% to 25%, then the curve increases again.
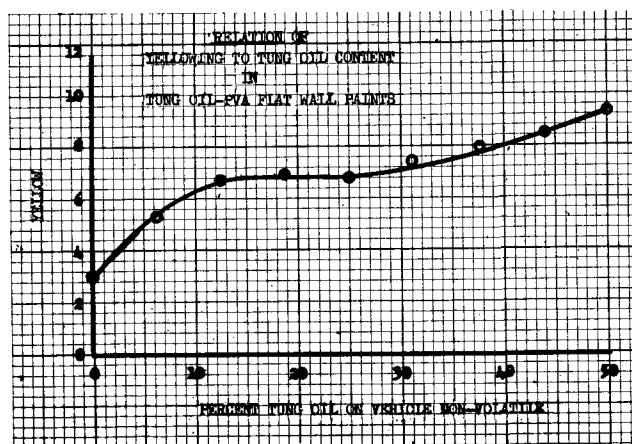

Fig. 4.

At the time we applied the emulsion series of paints, we also used a conventional alkyd flat wall enamel on two panels; one was air-dried and the other baked 24 hrs. at 220°F., and the yellow color was measured. The amount of yellowing of the alkyd panel was measured at 14.5, which is much greater than any of the tung oil-PVA paints examined.

In conclusion, we would like to point out that we are attempting to regain the market we lost because of two wars and consequent high prices by developing new uses wherein we hope to make a contribution to quality and merit and not necessarily to lower cost.

Driers for Drying Oils

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THERE IS NOTHING in the world that so challenges man's scepticism as a "Wet Paint" sign on a newly painted surface. His disbelief can only be satisfied by his own tactile experience. If the paint is dry, he is invariably disappointed. If the finger comes away sticky and colored, he is ruefully annoyed but at least he has verified what he has been warned against.

He little knows or cares that millions of dollars are spent annually to insure him that paint will dry.

That there is scientific equipment to test the drying time of a paint is an irrelevancy (1). Nor is he aware that the oils, varnishes, or alkyds in a paint are laboratory-selected with almost as much care as is his food. His prime concern is whether or not the paint dries.

Through experience the average person realizes that paint does dry. He has, although he may be scientifically naïve, two built-in insurance clauses: the vehicles with which paints are made and the catalysts. For our purposes the vehicles emphasized will be drying oils, and the catalysts discussed will be the metallic soaps or driers.

The oils most used by the paint industry are linseed, tung, soybean, dehydrated castor, oiticica, safflower, fish, tall oil, and occasionally perilla. They are mixed glycerides of saturated and unsaturated fatty acids, and their properties depend upon the types and proportions of the component acids. These oils dry chiefly by the addition of oxygen at the unsaturated bonds.

With the exception of tung, oiticica, and fish oils, the oils used to make a paint are mixtures of palmitic, stearic, oleic, linoleic, and linolenic acids with minute amounts of arachidic (20C), lignoceric (24C), and other acids.

Tung oil, a triply conjugated 18-carbon acid, contains a large quantity of elaeostearic acid.

Oiticica oil contains licanic acid, an 18-carbon acid with one keto group. In other respects it is identical with the elaeostearic acid present in tung oil.

Fish oils contain highly unsaturated, straight-chain acids of 20-, 22-, and 24-carbon chain lengths. Menhaden oil has as one of its principal acids 17% of clupanodinic acid, a 22-carbon chain acid with 5 double bonds.

The drying efficiency of an oil is generally expressed by the iodine number. This iodine number indicates the degree of unsaturation of a fat or oil as determined by allowing a known weight of the material to react with iodine, in this case the number of grams of iodine combining with 100 g. of fat or oil. Theoretically the higher the iodine number, the better the drying qualities of the oil. In the case of conjugated oils, such as tung or oiticica, the iodine number is not a measure of true saturation for these oils dry faster than some of the other oils with a higher iodine number. It has been suggested that the compositions of the oils should be used in determining their drying powers, not the iodine number. Thus, in England, Hilditch (2) and Greaves (3) formulated a "quick-drying index."

This drying index formula is based on the linoleic and the linolenic contents of the oils.

Hilditch's formula is $\dfrac{(\text{Len})(\text{Lin} + \text{Len}) = \text{D.I.}}{100}$

Greaves' formula is $\text{Lin} + 2\,\text{Len} = \text{D.I.}$

Lin = % linoleic acid
Len = % linolenic acid
D. I. = drying index

Typical drying-index values are (4):

Oil	Lin	Len	D. I. (Hilditch)	D. I. (Greaves)
Tung	10	77	....	164
Perilla	5	68	50	141
Linseed	20	50	35	120
Dehydrated castor	87	....	....	87
Soya	50	9	5	68
Safflower	67	....	....	67
Tall oil fatty acids	48	5	....	58
Tall oil fatty acids	45	....	....	45

For the paint industry the more important drying oils can be classified in the following groups (5): I. linoleic oils, II. linolenic oils, III. conjugated oils, IV. miscellaneous, and V. tall oil.

I. Linoleic Oils

This group includes oils containing more than 50% of linoleic acid, based upon the total fatty acid content, with iodine values ranging from about 120–170. Typical fatty acid compositions—percentage by weight are given in a tabulation.

Oils	Iodine No.	Saturated	Oleic	Linoleic	Linolenic
Soybean	125–140	17	24	50	9
Safflower	140–150	10	13	77	..
Tobacco seed	135–147	10	15	75	..
Grape seed	133	12	17	71	..

II. Linolenic Oils

The distinction between oils in the linoleic and linolenic groups is an arbitrary one since both acids may be present in either.

The more important oils with the highest linolenic content are given in detail.

Oils	Iodine No.	Saturated	Oleic	Linoleic	Linolenic
Linseed	170–200	9.5	19.0	24.1	47.4
Perilla	193–204	9.5	18.0	......	72.5
Stillingia [a]	146–188	9	10	30	45

[a] Stillingia oil now being used in Europe is obtained from kernels of the Chinese "tallow tree" and is used in China for making soaps and candles.

III. Conjugated Oils

The conjugated oils, to over-simplify a definition, are the known standard oils whose double bonds have been conjugated or isomerized either by heat or chemicals.

IV. Miscellaneous

Fish oils are derived from sardines, menhaden, whale, herring, and pilchard.

Castor oil, which is not a drying oil in itself, is made so by dehydration, giving a "conjugated" oil.

For want of a better place the polyurethanes are included. Many of the urethane polymers offered to the paint industry are oil-modified and will combine with most of the standard drying oils now used.

V. Tall Oil

Tall oil is not a natural drying oil but is a by-product of the wood pulp industry. It is a mixture of fatty and resin acids together with about 10% of unsaponifiable matter. The fatty acid mixture contains oleic and linoleic acids.

Mechanism of Oil Drying

There are many theories, all having some validity, on how oils dry.

Most oil films dry naturally through polymerization and oxidation. Addition of metallic driers accelerates this drying. A simple explanation of polymerization is that during the process the oil molecules combine at the double bonds of the unsaturated fatty acids to form larger molecules. Eventually this molecular growth produces a viscous film that will turn solid. Polymerization can be accomplished without oxidation. Oxidation is the absorption of oxygen at the double bonds of the unsaturated fatty acids. Eventually oxidation leads to polymerization.

It has been suggested that there are four steps in the formation of a film; inhibition, peroxide formation, peroxide decomposition, and polymerization (6).

During the induction period no significant oxygen is absorbed by the oil. Peroxides begin to form as soon as oxygen begins to be absorbed. These inter-

mediate peroxides readily decompose into free radicals, which initiate the oxidation and polymerization reactions. Driers accelerate these reactions, particularly cobalt and manganese, since their ions behave both as oxidant and as reducing agent (7).

As with the oils, there are also many theories as to how these driers work. The way a film will dry is dependent upon many factors. Temperature, moisture, light, the metals, and the amount of metals used, to mention but a few items, can influence drying.

The present-day oil-soluble and compatible drier bears little resemblance to its predecessors, the "cooked-in" drier and the "aged" drier, wherein metallic oxides were introduced directly into the paint. Autoxidation and sludging have been virtually eliminated. Moreover drier manufacture is now rigidly controlled to meet definite A.S.T.M. specifications (8) (Table I).

TABLE I
Naphthenic Driers—Specifications and Typical Properties

	Cobalt	Lead	Manganese
% Metal	6.0 ± 0.1	24.0 ± 0.1	6.0 ± 0.1
Viscosity (Gardner)			
Spec. (max.)	A	A	C
Typical	<A	<A	A
Color (Gardner)			
Spec. (max.)	Purple	10	17
Typical	Purple	8	16
% Nonvolatile			
Spec	48–58	55–70	50–65
Typical	52–55	60–65	55–60
Specific gravity (25°C.)	0.94	1.15	0.95
Density, lbs./gal. (25°C.)	7.84	9.59	7.92
Flash point, °F. (TCC) (min.)	100	100	100
Solubility (25°C.)			
Mineral spirits 1:10 by wt.	......	Permanently miscible	......
Raw linseed oil 1:19 by vol.	Miscible	Miscible	Miscible

Of the various acid carriers for drier metals, the three important ones are naphthenic acid, 2-ethylhexoic acid, and the tall-oil acids.

In the paint industry the naphthenate driers are at present the most popular. The refined naphthenic acids with which driers are made usually have an acid number of 220–260. Since naphthenic acid is a good wetting-agent, its use imparts a slight flow to the products.

The naphthenate driers have taken precedence because originally they showed greater solubility in oils, thinners, and alkyds. They did not oxidize readily and allowed for greater metal combinations than other acids. To some extent most of these advantages have disappeared.

A good example of progress is the tall-oil driers now being marketed. These are driers of excellent stability and color, metal contents are equal to those of the naphthenates and octoates, and most are practically rosin-free. Moreover they are less expensive than naphthenates.

In a choice between naphthenates and tallates it should be remembered that the former act as good wetting-agents whereas the latter do not. Moreover tallates cannot be used in Government Specification paints that prohibit "rosins."

The octoate driers, which are the most expensive, are, in a sense, specialty driers. They are made from 2-ethylhexoic acid, which is an odorless acid; consequently the octoates can be used in odorless paints. Because the acid is practically water-white, octoate driers are used where color is a factor. For example, some vehicle-makers who add driers to their products

find that these driers give lighter colors than other types. Too, some paint manufacturers stipulate cobalt octoate for less discoloration in their high-priced white enamels. One manufacturer of silicone resins recommends octoate driers as best for catalyzing these resins. Under conditions where extreme humidity is a factor, films will reach a quicker tack-free time with octoate driers. With some alkyds the drying time has been cut in half over that obtained where either naphthenates or tallates have been used.

Printing-Ink Driers

The printing-ink industry requires some variations in the vehicles carrying the drier metals. While the paint driers are cutbacks of acid soaps in petroleum solvents, printing-ink driers are made from soaps of fatty acids or rosin dissolved in a drying oil. The principal raw materials, other than the metals, are raw linseed and soybean oils or fatty acids, rosin, heat-bodied linseed oils (litho oils), and tall oils.

A slight change in the viscosity of a drier may change the consistency of an ink so as to make it unsuitable for use. Because of these special consistency requirements most ink driers are compounded from more than one-viscosity oil. The thin-bodied oils are employed for shortness and penetration, medium oils are used for wetting and flow, and the heavy oils give tack and body to the ink and also the driers.

Individual Driers

Of the many metals listed in the periodic table of elements only six seem to predominate as driers. These are lead, cobalt, manganese, calcium, zinc, and iron.

Lead

Lead is known as a "through" or bottom drier and is obtainable in solutions having 16% or 24% lead as metal. It promotes drying by polymerization and, if given enough time, it could be the only metal used. Even now it is used more than any other drier metal. The amounts incorporated vary from 0.1 to 5.0% metal, depending on the vehicle and product.

Lead naphthenate may be added to the mixing paste so that advantage can be taken of its wetting properties for pigments that are hard to grind. It is also a rust inhibitor.

Although it is a universal drier, certain precautions must be taken with lead. It should not be used in aluminum coatings because it will destroy leafing, but there are specialty aluminum finishes where leafing is undesirable and lead can be used. Nor is lead advisable where sulfur fumes are present; there is the likelihood of a paint darkening because of the formation of lead sulfide. A third prohibition against lead is its use in toys and baby-furniture paints. Some state laws that require paints to be labelled as containing "poison" if they have more than 1% lead metal prevent some people from using it. Rarely, if ever, is the 1% lead content attributable to the drier.

Calcium

Calcium, available in solutions bearing 4% or 5% calcium as metal, for years had never been considered a drier. Many chemists refused to use it because they believed it injured the water resistance of a film. But when it was introduced as a naphthenate, it was found to have some unusual properties. First and

foremost was its effect on lead driers. Vehicles such as alkyds and phenolic varnishes made with oiticica or tung oils, would haze and lose dry when lead was part of the drier system. The introduction of a small amount of calcium naphthenate stabilized the lead by preventing its precipitation, thus maintaining drying efficiency as well as preventing hazing.

During World War II and the Korean War, when cobalt was allocated to the paint industry, it was found that with calcium naphthenate only half the amount of cobalt normally used was necessary.

Calcium is now used as a replacement for lead in those finishes where lead is not advisable.

Like lead, calcium can be added to the mixing paste. It is a good wetting agent for hard-to-grind pigments and in many cases helps overcome loss of dry. As a wetting agent calcium naphthenate will help prevent "blooming" and "silking" while calcium octoate is effective in forestalling "gas checking" or "frosting."

Cobalt

Unquestionably the most powerful drier metal available to the paint chemist is cobalt. It can be obtained in solutions of 4, 6, or 12% cobalt as metal. It is the one drier that must be used most cautiously and should be added on the thin-down of the paste.

Cobalt is a "top" drier, i.e., it is an oxidizing drier working at the surface of a film, and the amounts used are small, usually from 0.005 to 0.2% of cobalt metal based on the vehicle solids. Excessive amounts of cobalt will cause wrinkling in a film. Although this wrinkling is desirable in some specialty finishes, it is not desirable in standard finishes. Should there be an overdose of cobalt, it can be rectified by adding zinc in two to three times the amount of cobalt present.

Cobalt naphthenate is also used as a catalyst, along with the usual peroxides, for curing polyester-fiberglas reinforced resins at room temperatures.

Cobalt driers are used extensively in printing inks since they are the most effective. The amount of cobalt in the ink is critical. An excess of cobalt will produce too hard a surface for over-printing in multicolor processes; too small a percentage of cobalt will cause smudging of color. Printing-ink driers, unlike paint driers, have a wide range of metal contents. For example, cobalt paste driers are available with 1.8, 2.1, 3.6, 4.6, 5.6, and 6.0% cobalt.

Manganese

Manganese, obtainable in 4 and 6% solutions, is one of the most useful drier metals, but it is used sparingly, primarily because of its color. The "staining" factor of manganese particularly limits its use in white paints. Were it not for that, it would be used much more extensively. It is both an oxidizing and polymerizing metal, combining the characteristics of lead and cobalt. Thus it gives a through and surface dry at the same time. Nonetheless it cannot be used alone because the resultant film will be hard and brittle. The amount used will range from 0.005 to 0.2% metal.

Bake finishes frequently employ small amounts of manganese, ranging from 0.005 to 0.03%. Like cobalt, manganese is added in the thin-down of the paste.

For printing inks the metal contents vary, i.e., 3.5, 5.6, 6.0, 6.5, 7.0, and 8.2%.

Zinc

Zinc is both an auxiliary drier and an excellent wetting agent. As a drier it helps films to dry harder because it holds the film surface open longer, thus allowing more oxygen to be absorbed by the film. Some lead-free formulations have successfully incorporated zinc along with calcium and cobalt. As a wetting agent, zinc naphthenate will shorten the mixing and grinding time of such pigments as toluidine reds, cadmium reds, and iron blues.

Iron

Iron, like manganese, is one of the drier metals whose use has been hindered in a large measure because of its color.

For years iron served, probably not knowingly, as a drier. Varnishes cooked in the old iron kettles had incorporated into them enough iron to serve as a catalyst. Some of the old drier formulas contained iron oxide as part of their ingredients. Later iron was the principal catalyst in bake finishes, particularly in the manufacture of patent leather. It was not considered as an effective air-dry metal.

With most medium- and long-oil aluminum vehicles, iron, in combination with cobalt, will contribute toward obtaining a through dry to aluminum films. Here iron does what lead should do but without loss of leafing. In paints pigmented with iron oxides or carbon blacks, iron naphthenate will eliminate, either partially or completely, loss of dry. The after-tack in paints made with fish oils may be cured with iron drier.

As a wetting agent, iron naphthenate will help obtain quicker and better grinds and consequently better glosses in carbon black-pigmented finishes.

It will help eliminate the "orange-peeling" that sometimes occurs when a carbon black finish is baked on metals, as in the automotive industry.

Other Metals

There is hardly a metal in existence that has not been examined for its drying effectiveness. Some show possibilities; many have fallen by the wayside.

Vanadium has drying powers equal to that of cobalt, but because of its bad staining qualities and the difficulties encountered in preparing an efficient compound it is not yet commercially practical.

The rare earths, such as cerium or cerium and lanthanum combinations, are excellent in finishes baked at 300°F. and above. In air-dry finishes the cerium type of drier is not too efficient.

Zirconium, which is actually not a drier but a catalyst for other metals in air-dry finishes, works something like zinc in that it keeps the film open longer, which means a longer tacky period. It is extremely effective in force-dry finishes, i.e., between temperatures of 180°–240°F. It is also helpful in maintaining gloss, according to some authorities.

Drier Calculations

From earliest times it has been recognized that a single drier metal alone is not as effective a catalyst as a combination of two or more metals. The manufacturer of the paint or varnish usually mixes his own combinations. What these mixtures are depends on the type of vehicles used. As a rule of thumb, we always have the standard combination of 0.5% lead,

0.05% cobalt, and 0.02% manganese based on the total vehicle-solids in the paint. In paints made with varnishes the solids calculations are made on the pounds of oil in the varnish; in the case of alkyd resins, on the pounds of resin in the alkyd.

Calculations are simple. For example, given 100 lbs. of oil, the requirement is to add 0.5% Pb; 0.05% Co; 0.02% Mn. The driers to be used are 24% lead, 6% cobalt, and 6% manganese. The formula is given thus:

$$\frac{(\text{lbs. of oil}) \times (\text{conc. of metal required})}{\text{concentration of drier used}} = \text{lbs. of liquid drier required}$$

$$\text{lead} \quad - \quad \frac{100 \times .005}{.24} = 2.08 \text{ lbs. lead drier}$$

$$\text{cobalt} \quad - \quad \frac{100 \times .0005}{.06} = .833 \text{ lbs. cobalt drier}$$

$$\text{manganese} \quad - \quad \frac{100 \times .0002}{.06} = .33 \text{ lbs. manganese drier}$$

Figure 2 can be used as a handy reference guide for determining drier dosages.

Now as to the amount of driers used for any given formula, there is considerable aid from the many suppliers of the various vehicles. Their efforts to give the industry exacting details of the chemical and physical properties of their products have resulted in a series of drier recommendations that serve as good starting points. Tables II and III list some of the recommendations suggested by the vehicle suppliers (11, 12).

The use of driers with these oils and alkyds is fairly routine although modifications and combinations of these vehicles may cause some problems. It must be remembered that these recommendations are for unpigmented vehicles. In practice, when pigments are present, slightly more drier is used.

More complex is the drying of the epons, the silicones, the conjugated oils, and the styrenated alkyds,

TABLE II
Drier Recommendations for Alkyds

Type of oil	% Metal on oil			Remarks
	Co	Pb	Mn	
Linseed, blown or heat-bodied	0.03	0.25	....	....
Linseed, raw	0.02–0.03	0.20–0.25	....	....
	....	0.20–0.25	0.02–0.03	....
	0.03–0.04	....	....	....
	....	0.15	0.01	"Boiled Oil" 16-hr.-dry
	0.015	....	0.02	"Boiled Oil" 16-hr.-dry
	0.01–0.03	0.3–0.6	0.02–0.04	Exterior white paints
	0.025–0.05	....	0.025–0.05	Iron oxide paints
Linseed, refined	0.02	0.15–0.20	....	....
	....	0.15–0.20	0.02	....
	....	0.10	0.01	"Boiled Oil" 16-hr.-dry
	0.01	....	0.02	"Boiled Oil" 16-hr.-dry
Oiticica	0.03–0.10	0.3	0.0–0.03	....
Perilla	0.02	0.15	....	....
Safflower	0.05	0.5	0.02	....
Tung	0.02–0.04	0.15–0.40	....	....
Dehydrated castor, bodied	0.03–0.10	0.2–0.5	0.0–0.02	....
Fish, bodied	0.04–0.08	0.5–0.8	....	....
	0.05	....	0.05	0.3% Fe for dark paints
Fish, pressed	0.05–0.10	0.2–0.5	....	For high stearin content oil use low Pb, high Co
Fish, refined	0.05	0.5	....	....
Soybean, blown	0.05–0.10	....	....	....
Soybean, heat-bodied	0.05–0.10	....	....	....
Soybean, raw	0.02–0.03	0.4–0.5	0.03–0.07	....
Tall oil	0.01–0.05	0.5–1.0	....	....

TABLE III
Drier Recommendations for Alkyds

Type of oil	Driers, % metal on NV				
	Length	Ca	Co	Pb	Mn
Dehydrated castor	Short	....	0.05	0.3–0.6	0.0–0.3
	Med.	0.1	0.05–0.07	0.4–0.7	....
	Long	....	0.05–0.10	0.5–0.8	....
Linseed	Short	....	0.05	0.3–0.5	0.03
	Med.	....	0.03–0.05	0.3–0.5	0.03
	Long	....	0.02–0.05	0.5–0.8	0.02–0.03
Soybean	Short	0.1	0.05	0.1	0.03
	Med.	0.1	0.01–0.05	0.2–0.3	0.0–0.03
	Long	0.1	0.03–0.07	0.3–0.6	0.0–0.03
Tall oil	Med.	0.0–0.5	0.05–0.10	0.0–0.2	0.0–0.02

For baking, 0.01–0.02% Co.

and other chemically treated copolymers. Some of these do not require driers, others only minute amounts.

Epons

The epons, which can be used for air-dry or bake finishes, require driers only for air-dry purposes. A catalyst, such as triethylamine, is usually present. With some epons 0.05% cobalt has been found helpful in a pigmented finish.

Silicones

As previously mentioned, the octoate driers seem to give the best results with silicone resins.

Cobalt (0.02–0.05%), zinc (0.05%), and manganese (0.01–0.05%) are considered safe driers because of their weaker catalytic action on the silicones. Usually these three can be added to solutions that contain 50% or less of the silicone resin without causing undue gelation and thus cutting down on the shelf life of the paint. Lead (0.01–0.1%) and iron (0.01–0.02%) can be used but with caution. Lead is a fast-curing agent and should be added only at the time the material is to be used, otherwise it will shorten the heat life of the resin and may cause gelation. The warning about lead may be extended to the container. If the container is soldered and unlined, the lead in the container may act as a catalyst for the resin. Iron too should be added in small amounts because it may promote gelation in the container.

Conjugated Oils

Films cast from conjugated or isomerized oils without driers show frosting and wrinkling. Driers prevent this. Because of the differences in the oils, i.e., linseed oil vs. isomerized linseed oil, the drier combinations will vary. For example, a formula effective in linseed oil will not work with isomerized linseed oil, but the reverse can be true.

	Pb	Co	Mn	
Linseed oil	0.2%	0.02%	0.5%	(poor for I.L.O.)
I.L.O.	0.3%	0.03%	0.01%	(good for both)

Theoretically, given the best drier combination, isomerized linseed oil dries five to eight times faster than ordinary linseed oil.

Pigments affect drying times of conjugated oils. Chrome yellow, lithopone, zinc yellow, zinc green, zinc chromate, and Prussian blue slowed drying time in isomerized linseed oils and tung oil. By replacing a drier combination of 0.3% Pb, 0.033% Co, 0.01% Mn with only 0.15% Co, dry time was cut from one-

half to two-thirds the time with the other driers. The explanation given is that these pigments probably containing Zn, Mn, or Fe exert some negative catalysis (13).

Styrenated Alkyds and Other Chemically-Treated Copolymers

Styrenated alkyds for air-dry finishes employ the standard combinations of lead and cobalt. The amounts used are much less than those in conventional finishes. The ranges vary with the types of treated oils and their particular uses. Based on the nonvolatile, the amounts suggested have wide latitudes:

cobalt	0.0125%–0.1%
lead	0.1% –0.8%
manganese	0.1% –0.04%

If oils, such as castor, fish, soya, or safflower, are present, small amounts of calcium (0.1–0.2%) are advised as supplementing driers.

Polyurethane Coatings

The drier needs of polyurethanes generally follow those of the conventional drying oils. Usually 0.4% lead and 0.04% cobalt will serve to air-dry a polyurethane finish. Bake finishes will cure without driers, but additions of small amounts of manganese or cobalt (0.01–0.02%) will give harder films.

A few of the polyurethanes will air-dry with the use of various amines.

Emulsive Driers

Although we have discussed driers with respect to drying oils and alkyds, they are also used in some water-emulsion paints, particularly with such latices as styrene-butadiene. Moreover driers are a necessity with latex paints that have been oil- or alkyd-modified and with emulsifiable oils and alkyds. The standard driers are fairly efficient, but formulation complexities have resulted in special driers tailored for emulsion paints. Two drier manufacturers are marketing such catalysts under the trade names of "Emulsive Driers" (9) and "Cyclodex Driers" (17).

Emulsive driers, unlike conventional driers, may be introduced at any stage in the production of latex emulsion paints and their oil or alkyd modifications. These driers readily disperse through the batch, without any tendency to agglomerate in the water phase. They can also be used in typical oleoresinous or alkyd finishes.

The emulsive driers are manufactured in the standard concentrations, 6% cobalt, 24% lead, and 6% manganese, which are employed in today's paint formulations. Thus the quantity of emulsive drier required may be calculated in the conventional manner. There is no need for reformulation by the paint manufacturers.

Loss of Dry

A problem that constantly plagues the paint and ink industries is the loss of dry with aging. It has been postulated that this results from adsorption of the drier by the pigment because of the strong molecular forces of attraction in the pigment surface toward the metal compounds of the driers. Among the pigments affecting drying are carbon blacks, titanium dioxide, ochres, iron oxides, Prussian blues, chrome green, china clays, and asbestine.

COBALT & MANGANESE DRIERS

Pounds of Drier Solution Required for 100 Pounds of Oil or Alkyd Solids
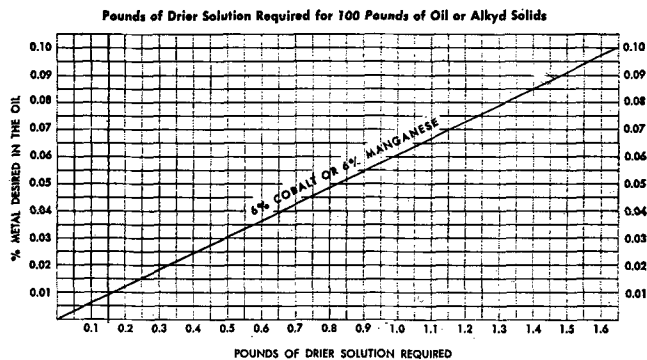
These charts are based on the drier metal percentage necessary for the total amount of the drying oil (or oils) in the formulation. For alkyds, the required percentage of drier metal is generally calculated according to the amount of resin solids present.

LEAD, ZINC, CALCIUM DRIERS

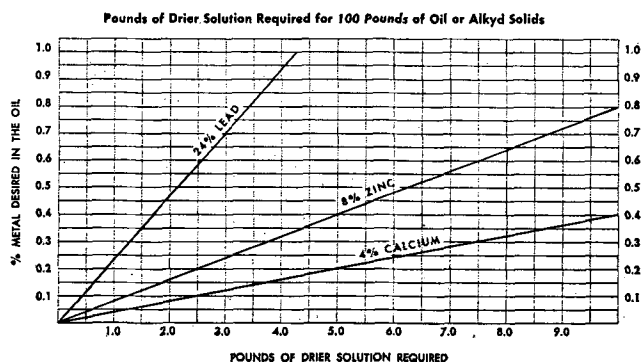Pounds of Drier Solution Required for 100 Pounds of Oil or Alkyd Solids

FIG. 1. Guide for determining drier dosages.

The ink industry has found that certain alumina hydrate lakes are subject to this loss of dry. There may be other factors, moisture may be present, the pigments may be acidic in nature, there may be a dry-inhibiting wetting agent present, such as Turkey Red Oil (14).

Some salts and acids will retard the drying time of lithographic varnishes and inks. The drying efficiency of lead and manganese is diminished in linseed oil and linseed oil varnishes that contain phosphates, sulfates, silicates, or borates. Cobalt however is not affected (15).

Investigation of drier adsorption by the Philadelphia Production Club in cooperation with various raw-material suppliers has brought to light some interesting facts. Work was done with titanium dioxide and carbon black. There was no significant difference between the adsorption capacities of rutile and anatase TiO_2. A treated white, i.e., titanium dioxide treated with either alumina or aluminum silicate, will absorb 50% of the drier present. An untreated white will absorb 65% of the drier. By percentages cobalt, calcium, and manganese are adsorbed twice as much as lead.

Adsorption for TiO_2 is very rapid in the beginning, and this holds true for carbon blacks where drier adsorption duplicates the behavior of white pigments.

There is strong evidence that driers do not lose their catalytic activity by being adsorbed. Perhaps this adsorption is a reversible process. Actually paints that have lost their drying efficiency usually can be made to dry by regrinding (16).

The question is how to overcome this loss of dry. One way is to add excess drier although this can be

dangerous. The addition of 3 to 5 lbs. of litharge to a 100-gal. batch of paint, where litharge can be tolerated, will serve as an antidote. Litharge is exceptionally effective in carbon-black paints.

Calcium or zinc naphthenate will help with white paints while iron naphthenate will do a good job with carbon blacks and iron oxides.

There are some proprietary products on the market that claim to diminish loss of dry by acting as feeder driers, such as Nuact Paste, which contains a minimum of 44% lead. Cobalt HR-254, a paste compound containing 21.0% cobalt as metal, has been recommended as an addition to inhibit loss of dry in lead-free systems (17). Cobalt hydrate, a dry powder with a cobalt metal content of 62%, is beginning to find favor for similar purposes (18). Another catalyst, nonmetallic in composition, is Activ-8. It is composed of o-phenanthroline, 2-ethylhexoic acid, and n-butanol and is extremely expensive compared to standard driers. But it is claimed that only minute amounts are needed to activate other driers. It seems most effective with manganese and cobalt (19). None of these "feeder driers" actually replace the normal amounts of driers needed.

Conclusion

Research is constant for better driers. It may be recalled that triethylamine is used as a catalyst for air-drying of epon resins. Other studies have uncovered amines which prevented excessive loss of drying on aging in certain pigmented vehicles and have boosted the efficiency of the other drier metals (20). In 1958 a patent was granted to a drier accelerator composed of "either iron, lead, or manganese soap and various amines" (21). To show how extensive this research is, some of the many projects are reported.

An oil-soluble hemin oleate which worked well as a catalyst (in linseed oil) was produced and was particularly active in pigmented systems; of course, hemin is obtained only at a prohibitive price.

Work has been directed toward complexes (combinations) synthesized around a central metal. This is a costly proposition. There are other restrictions besides economics, on the uses of complexes. Cobalt, for example, has resisted improvement by complexing. The relationship between a complex drier and the components of an oleoresinous system is less predictable than when the conventional driers are used. Occasionally a product of different physical characteristics has resulted from the use of a complex (20).

It has also been noted that pure chlorophyll acts as a drier and anti-skinning agent in linseed oil (22).

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Drying Oils in Varnishes

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OUR EARLY KNOWLEDGE of varnishes (1) is derived from documentary evidence and preserved specimens which have come through the ages not necessarily in their original form. The surviving records are heterogeneous and have been subjected to changes brought about by the writers' whims and idiosyncrasies. These include recipes and various descriptions of coatings and works of art.

The early artists painted with oleoresins, linseed oil, gums, glue, and the like. The use of oil varnishes and resins is described by Theophilus in the 11th century. In the 9th century Eraclius described a preparation of linseed oil treated with lime and litharge. These finishes were used largely on works of art, the trade for which was stimulated by the prosperity of the era. The Van Eycks are generally credited with being the first to realize the advantages of oil media and were the first to use oils on a large scale.

Varnishes found uses in larger volume in furniture and home finishing in the 16th century. In this period the way of European life changed, and people took more pride in home decoration and consequently de-

manded more finishes. During this same period highly finished art objects were being introduced from the Orient. These were known as lacquer ware. In 1773 the first printing of Watin's book on the subject of coatings appeared. It contained innumerable formulae on varnish making, some of which are not too far different from those in use today.

The 18th and 19th centuries were the beginning of our modern varnish era. With the turn into the 20th century China wood oil (2) was introduced, followed by phenolic resins, one of our first synthetics.

It is not uncommon today to find references in the literature in which violin makers are much concerned about duplicating the finishes used by the old Italian masters. Apparently our modern varnishes omit certain properties desired by them.

Definition of Varnish

Historically varnishes have been discussed in general terms. However, to clarify any discussion of drying oils and varnishes, it is imperative that the term