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).

REFERENCES

1. Errico, A., "Paint Varnish Production," private communication: there are at least seven drying-time instruments (1959).

2. Hilditch, T. P., J.O.C.C.A., *31* (1948).

3. & 4. Greaves, J. H., Oil & Colour Trade Journal, *113* (April 1948).

5. Mills, M. R., "An Introduction to Drying Oil Technology," 1st ed., vol. 1, pp. 3–13, Pergamon Press Ltd., London, 1952.

6. Mueller, E. R., "Paper H12, A.C.S. Division of Paint, Plastics, and Printing Ink Chemistry."

7. Bawn, C. E. H., J.O.C.C.A., *40* (Dec. 1957).

8. A.S.T.M. Standards, Part 4, pp. 220, 251, 556, AS.T.M., Philadelphia, 1952.

9–12. "Witco Driers," Witco Chemical Company Inc., New York, N. Y.

13. Von Mikusch, J. D., Official Digest, *372* (1956).

14. Mace, D. M., and Walker, W. C., "Loss of Drying on Aging Properties of Hydrate Lakes," National Printing Ink Institute, Lehigh University.

15. Coupe, R. R., J.O.C.C.A., *40* (December, 1957).

16. Philadelphia Production Club, paper to be presented in Atlantic City, October, 1959.

17. Nuodex Products Company Inc.

18. Witco Chemical Company Inc., New York, N. Y.

19. R. T. Vanderbilt Company, New York, N. Y.

20. Zettlemoyer, A. C., and Myers, R. R., papers 2 and 3, A.C.S. Division of Paint, Plastics, and Printing Ink Chemistry, Chicago (September, 1953).

21. Meyers, R. R., and Zettlemoyer, A. C., (Harshaw Chemical Co.) U. S. 2,852,405 (1958).

22. Sevestre, J., Peint. Pig. Vernis., *31* (1955).

Drying Oils in Varnishes

A. E. RHEINECK, North Dakota Agricultural College, Fargo, North Dakota

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 demanded 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 varnish should be defined. This is especially true in today's ever-changing coatings technology.

The definition of varnish is not the same today as it was years ago. The old varnishes are defined as being solutions or mixtures of drying oils and varnish resins, which are usually combined by a cooking process and then thinned to a workable viscosity with a volatile solvent. Further the varnish should dry to form continuous serviceable films by oxidation or polymerization or both.

The solubility of a resin and oil is often mentioned. "Solubility" in this instance is a broad term and means a true solution or a dispersion of resin in oil.

Within recent years the term "varnish" has become generic to a broad class of coatings. It is not uncommon to find alkyd resins called varnishes. The term has further broadened to include oil-modified urethane coatings, polyester finishes, copolymer oils, hydrocarbon polymers, polymerized terpenes, decarboxylated rosin derivatives, silicon polymers, vinyl and acrylic esters, and esters based upon epoxy resins. As a class, this type of coatings materials derives its name not from the chemical composition, but from the end uses, general appearance, and performance characteristics, all of which are comparable to the classical varnishes.

Other papers in this symposium cover several of these coatings materials in greater detail. The subject-matter of this paper will therefore adhere more closely to the compositions required by the classical definition. Figure 1 illustrates the preparation of a classical varnish (3).

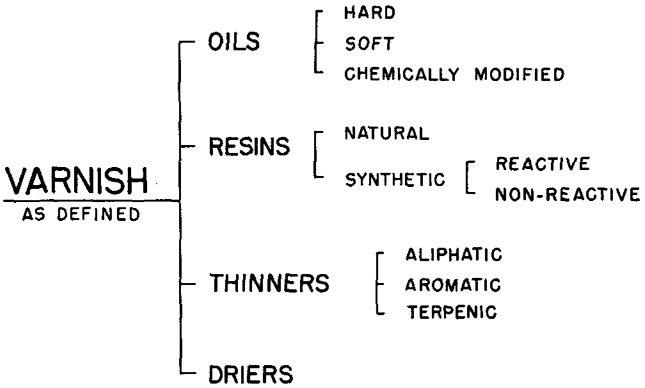

Fig. 1. Composition of classical varnishes.

With the advent of closed-kettle, alkyd resin processing in the late 1930's the cooking of varnishes turned to a revised form of combining the oil and resinous components. In this "uniphase" or the *in situ* process the base oil components, polyol and fatty acids, and the base varnish resin components, a rosin, polyol, and modifiers like *alpha-beta* ethylenic dicarboxylic acids and/or phenolic sirups, are changed to the reaction kettle in a definite order, cooked, and thinned to the desired viscosity (Figure 2). Essentially the final varnish of this reaction system is composed of the same basic raw materials as those shown in Figure 1, but there are in some instances differences in final performance characteristics. Economics and available kettle-capacity favored the conditions for the *in situ* process.

TABLE I

Hard Resins Produced for Use in Protective Coatings (4)

Year	Thousand pounds			Total
	Phenolic [b] all types	*Resin esters* [c]		
		Unmodified	Modified	
1941	34,230	....	....	34,230
1942	21,009	....	....	21,009
1943	15,519	....	....	....
1944	10,296	....	....	....
1945	39,210	65,977		105,187
1946	28,698	69,266	35,373	133,337
1947	22,078	70,496	39,862	132,436
1948	57,640	....	....	141,474 [a]
1949	40,483	55,192	4,750	100,425
1950	46,355	63,413	10,950	120,718
1951	43,914	62,985	9,290	116,189
1952	43,277	59,546	9,099	111,922
1953	28,210	39,396	63,996	162,268 [a]
1954	22,970	40,510	54,959	148,541 [a]
1955	28,501	37,591	63,378	162,920 [a]
1956	27,664	33,001	62,299	160,564 [a]
1957	46,759	32,428	28,540	107,727

[a] Includes others in addition to those listed.
[b] Includes unmodified and rosin-modified.
[c] In some cases phenolic-modified are included when not reported as phenolics.

Present Trends

The trends in the coatings industry are away from the uses of varnishes prepared as defined and are very definitely focused into new areas. Consequently there is not much new work on classical varnishes to be found in the literature over the last 15 years.

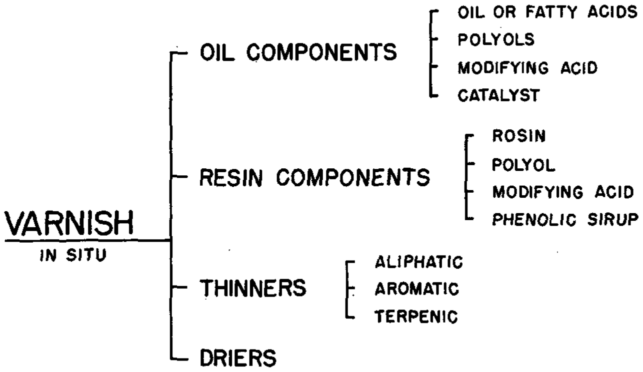

Fig. 2. Component parts of *in situ* or "uniphase" varnishes.

The consumption of all drying oils is reported by government agencies as the total used in paints and varnishes. Consequently it is difficult to arrive at figures on oils used only in varnishes. Tung oil is the only drying oil which can be assumed to be used largely in varnishes and enamel vehicles. Linseed, safflower, and soybean oils find their main uses in alkyd resins and paints.

The volume of oil used in varnishes can be approximated from figures on the consumption of such hard resins as the unmodified and modified phenolic resins, rosin esters, and natural resins as copal, Kauri, and the like. The import of the copal and Kauri types is now less than 10 million pounds annually and will not be considered in this discussion.

The figures in Table I, compiled from the Tariff Commission Reports (4), show the consumption of phenol and rosin esters used in the protective coatings industry for the period 1941 to 1957. The totals do not show any growth, rather seem to indicate a diminishing volume when compared to the population-growth curve.

The oil consumption in varnishes is some function of the hard resin weight. As an example, it can be assumed that the average varnish is about 25 gal. in length. This means that the total oil used in varnishes is about twice the weight of hard resins recorded in Table I. This might be interpreted to mean that, in 1957, 215 million pounds of oil were used in hard resin varnishes by the drying oil industries. This is about 20% of the total weight of drying oils produced, and of this volume about 35–40 million pounds were tung oil (5).

There has also been a downward trend in rosin consumption by the coatings industries as reflected by the data of Table II. This trend may result from a shift away from the *in situ* varnish type of processing. There is no way of determining the quantity of oil consumed in these varnishes.

TABLE II
Consumption of Rosin, Excluding Its Esters by the Paint, Varnish, and Lacquer Industry (6)

Year	Million lbs.	Year	Million lbs.
1940	65.7	1949	48.5
1941	90.6	1950	53.3
1942	68.7	1951	41.9
1943	65.7	1952	40.7
1944	69.2	1953	38.7
1945	52.7	1954	35.2
1946	59.0	1955	33.7
1947	58.6	1956	38.1
1948	57.5	1957	30.6

The "away-from-varnishes" trend started in the late 1930's. Up to this time China wood oil was the important varnish oil. In 1940 its rate of use amounted to 120 million pounds per year (2). Although the unavailability of this oil from the Orient was anticipated, the tung plantings started in the Gulf states in the late 1920's and early 1930's were too young to cope with the demand. This forced the industry to look elsewhere for new varnish materials and varnish-like vehicles.

In this same period rapid strides were being made in alkyd resin technology; consequently some alkyd resins were a logical substitute for the classically prepared varnishes. It was also in this era that the *in situ* process began with the replacement of the China wood oil in varnishes by drying oil fatty acids, glycerol, and maleic anhydride.

The growth of alkyd resins (Table III) from 1941 to 1952 is in keeping with the population growth curve, but from 1952 to 1957 the volume seems to be holding constant at between 440 and 460 million pounds per year. The lack of growth increase in the last five years may be attributable to the growth increase in other coatings compositions, such as the vinyls, acrylates, epoxy resins, and others.

TABLE III
Alkyd Resins Produced for Use in Protective Coatings (4)

Year	Thousand pounds				Totals
	Phthalic		Polybasic Acid		
	Unmodified	Modified	Unmodified	Modified	
1941	124,287		15,451		139,738
1942	89,200		....		154,899 [a]
1943	153,614		43,374		196,988
1944	127,083		....		127,083
1945	135,833		17,233		153,066
1946	166,350	21,681	47,712		235,743
1947	....	....	....		302,941
1948	179,292	59,975	4,634	35,636	279,537
1949	195,474	67,654	10,923	42,373	316,424
1950	250,444	82,539	15,641	53,340	401,964
1951	260,833	107,519	12,343	59,890	440,585
1952	255,200	100,697	11,808	54,502	422,207
1953	286,578	102,593	11,360	9,531	410,062
1954	286,751	94,292	15,646	13,322	410,011
1955	325,516	129,031	25,579	11,469	491,595
1956	287,821	103,989	8,531	12,291	412,632
1957	314,434	118,094	7,551	19,240	459,433

[a] Includes others not listed.

It is too early to state their volume at present, but there are two oil-based products which will no doubt find an important place in the coatings industry. These are the urethanes as described by Renfrew *et al.* (7) and Stanton (8) (Figure 3) and the epoxidized and polymerized drying oil products as described by Findley (9) and Greenlee (10) (Figure 4). Originally these were two package systems, but at present this is not necessarily the case.

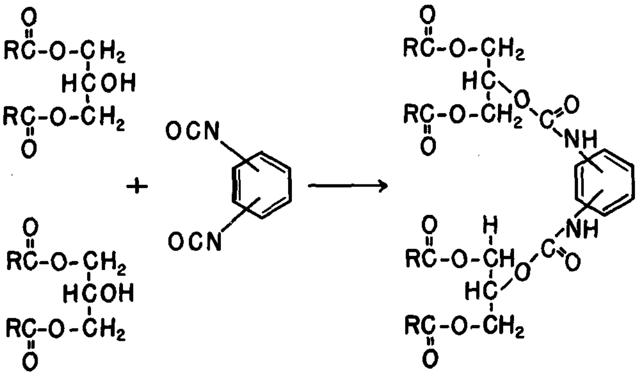

FIG. 3. Urethane oils.

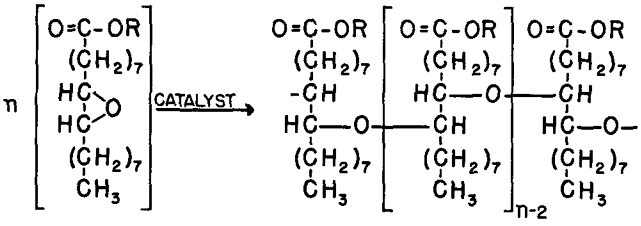

FIG. 4. Epoxy polymer.

These newer types of coatings no doubt prompted Kittle (11) in 1956 to introduce the term "Reaction Varnishes." Specifically these are two component systems in which a reaction takes place in the film, namely polyisocyanates (urethane coatings), ethoxylenamine adducts, and unsaturated polyester resins. However at present these are one-component systems.

It should be pointed out that today oleoresinous varnishes are still used but in a diminished volume. They are the victim of the progress of our time.

Varnish Oils

Oils used in varnishes comprise two classes, namely, those known as "soft oils" with isolated ethylenic groups, fish, linseed, safflower, tobacco seed, and soybean; and the "hard oils" with conjugated ethylenic groups, tung, oiticica, and dehydrated castor. The last-mentioned has properties intermediate between the "hard" and "soft" varieties. Some chemically modified oils are also included. The *in situ* process requires the above oils and their fatty acids, including the rosin-containing and rosin-free tall oils.

The "hard, soft, and chemically modified" oils may be used as a single oil component in a varnish. Alternately they may be used as a blend at the beginning of a cook or added as a "chill-back" oil. Usually "soft" oils are used in the latter. When "soft" oils are the only oil, it is preferable to use them in a prebodied form.

Tung Oil. This oil possesses certain inherent advantages not found in other oils, namely, fast kettling time, the formation of end products with desirable properties when correctly processed with the proper resins. The disadvantage is the formation of a frosted film when dried in a foul atmosphere; correct processing will obviate this. Tung oil and its varnishes were therefore taken as a standard of comparison during the period when substitutes were being sought.

The years 1938 to 1945 were critical for the varnish maker. The specific oils and products to which he turned are described subsequently. Conclusions from this work at that time caused people to say "there is no substitute for China wood oil, they are merely replacements."

Oiticica Oil. A semi-solid, green-colored, oiticica oil was introduced into this country from Brazil in the late 1930's. Since it resembles China wood oil quite closely, it was considered as a substitute. Varnishes made with this oil were more brittle and shorter than tung oil varnishes of the same length. The weathering characteristics of these early varnishes were poor. Three reasons may have been responsible for this, namely, the quality of the oil, processing temperature, and the composition of the oil.

The present oiticica oil is an amber liquid. This is known as "Cicoil," to distinguish it from the original semi-solid type. Lower processing temperatures are now recommended. With modified phenolic resins (12) the oil and resins should be cooked at 230–240°C., and with the less reactive resins 250–260°C. is suggested (13). Blends with dehydrated castor oil will overcome film brittleness. The embrittling characteristics are no doubt caused by the presence of the ketone group in its main component acid since it is known that oiticica acids can be resinified (14).

Dehydrated Castor Oil. Dehydrated castor oil was made by a number of different processes (15), but its varnishes, although color-retentive, never dried as hard as desired; in some cases varnish films showed syneresis on aging. This difficulty was corrected by the addition of various components to these varnishes as described by Wilson (16), or by the addition of oiticica oil.

Copolymer Oils. The linseed-cyclopentadiene copolymer oil was a tung oil substitute that was good. However, in general, the initial color was darker.

Chemically Modified Oils. In order to make acceptable varnish oils and, in general, oils with improved drying characteristics, the "soft oils" were modified with maleic anhydride or other *alpha-beta* ethylenic acids. These oils as a class are known as Clocker oils (17) or sometimes as nonphthalic long-oil alkyd resins. This method of upgrading has been used extensively on linseed oil, especially soybean oil.

These products can be considered as oils which are chemically combined with a maleic acid polyhydric alcohol ester. This immediately suggests two methods for their preparation. Clocker's process adds the maleic anhydride directly to the oil and this is esterified with a polyhydric alcohol, glycerol or a pentaerythritol. In emulsion oils and varnishes, ammonia or an amine is used in place of the polyhydric alcohol. In the alternate process (18) the oil is first alcoholized with the polyhydric alcohol and basic catalyst, then esterified with maleic anhydride.

This technique has been useful and economical for converting soybean oil to an oil resembling linseed in properties. Similarly linseed oil, in some instances, acquires some properties inherent in tung oil. In the former the maleic modification is 5% and in the latter about 10–12% when esterified with glycerol (15).

In terms of functionality this means that about 5% maleic anhydride (based on the oil), as the glycerol ester, is equivalent to the difference in iodine value between linseed and soybean oils of 45–50 or about one-half of the equivalent ethylenic group. Since modification and iodine values are based on 100 parts of oil, approximately 0.05 mole of glycerol maleate is equivalent to about 0.5 mole of ethylenic groups.

In one mole of linseed oil there are about six isolated ethylenic groups as compared to about 7 to 7.2 conjugated ethylenic groups in a mole of tung oil. Hence linseed oil modified with 10% maleic anhydride is about the same as 0.1 mole glycerol maleate, which is about equivalent to one ethylenic group per mole of oil. This appears to be in agreement with the soya-linseed equivalence mentioned above but does not take into account the increased functionality manifested in tung oil by virtue of the conjugation. The additional functionality equivalent to that due conjugation cannot be attained by additional maleic modification, hence the lack of complete equivalence of maleic-modified linseed and tung oil.

Nonglycerol Oils. It is a well-known fact in oil chemistry that improved properties may be obtained by replacing the glycerol with other polyols of increased hydroxyl functionality. To illustrate this point, linseed oil is taken as a control. This oil has an average iodine value of about 180 or the equivalent of two isolated ethylenic groups per fatty chain. It dries to a soft film with a characteristic "oil tack." Soybean oil, with an iodine value of about 130, or the equivalent of $1\frac{1}{2}$ ethylenic groups per fatty acid chain, forms a soft "cheesy" film. However the same soya fatty acids esterified with monopentaerythritol form a dried film about equivalent to a linseed film. This suggests the following functionality relationship:

$$\text{functionality product} = \begin{cases} \text{No. of polyol hydroxyl groups} \\ \times \text{ No. of ethylenic groups} \end{cases}$$

The "functionality product" for an oil equivalent to linseed is 6. For most oil work this relationship seems to hold fairly well. Based on the iodine value difference between linseed and soybean oils, 45-50, the functionality concept may be stated in another way, namely, one half of ethylenic equivalent is probably equivalent to one hydroxyl group.

Polyvinyl oleate made by the phenol technique (19) substantiates this relationship since it dries to a film of fair quality.

This can be taken a step farther, and one can speculate that an oleate of a polyol with 6 or more hydroxyl groups should be a film-former. Actually such an oleate has some film-forming characteristics.

This general concept is further and aptly demonstrated by Greenlee (20) with esters of epoxy resins. In this instance these resins are considered as highly functional polyols. Table IV illustrates the relationship existing between the number of ester groups in the final product and the number of ethylenic groups in the fatty portions of the molecule to obtain products with essentially identical 24-hr. dry. The functionality product derived in this instance agrees well with that obtained on the oils.

TABLE IV
Relationship Between Polyol and Ethylenic Functionality of Epoxy-Resin Linseed/Stearic Acid Esters (20)

Mols acid per mole alcohol		No. of ester chains per molecule	Av. No. of ethylenic groups	Functionality product
Linseed	Stearic			
3	1.5	4.5	1.36	6.12
3	4.2	7.2	.85	6.12
3	5.2	8.2	.75	6.15
3	6.5	9.5	.64	6.06
3	6.9	9.9	.62	6.14
3	8.3	11.3	.54	6.10
3	9.0	12.0	.51	6.12

Results in the early work with pentaerythritol *in situ* processing were encouraging to varnish makers. Consequently this polyol has found a definite place in several areas in the coatings industry, especially tall oil esters.

Isomerized Oils. Attempts have been made to duplicate the tung oil structure in other oils. The processes that have been used to produce the tung type of structure in linseed oil have been reviewed (15). With linseed and dehydrated castor oils the tung structure is only approached while with soybean oil a different oil was produced. The first two oils did show some improved properties as varnish oils, but the improvements were never as great as anticipated.

Table V indicates the composition of the above oils (15). These data show that it is theoretically impossible to produce the desired tung structure from soft oils without another reaction to increase the oil unsaturation. No good practical process is known at this time.

TABLE V
Composition of Oils Compared with China Wood Oil (15)

Oil	% Various acids				Total theoret. conj.
	Sat.	Mono-olefinic	Diole-finic	Triole-finic	
Soybean	13	28	54	5	59
Linseed	10	22	17	51	68
Dehydrated castor	3	7	87	3	90
China wood	5	8	4	83 [a]	87

[a] Actual composition.

All the methods and products suggested above as well as others (15) of lesser importance were used and tried. Each fulfilled its purpose in its time. Today dehydrated castor oil, copolymer oils, and oiticica oil are in limited use while tall oil and polyols of increased functionality are finding an ever-increasing market.

Varnish Resins. The types of resins conforming to the accepted varnish definition are, in some cases, quite difficult to justify. The art and technology recognize the natural resins and the synthetic resins mentioned in Table I. Alkyd resins are excluded since the resinous components are formed during the cooking process.

Epoxy resins might be included with varnish resins. Essentially they are highly functional resinous polyols and are used as such with fatty acids. Tess (21) evaluated these resins in the conventional varnish technique but concluded that these products were not as good as their esterification products.

Varnishes. The ultimate property to be achieved in any varnish is a high molecular weight, either by chemical or physical interaction or both, of oil and resin with such properties as drying time, film hardness, chemical resistance, and the like related to the amounts and functionalities of the basic components.

Oils and resins are unsaturated esters of high molecular weight. Two types of chemical reactions are possible, namely, ester interchange and a carbon-to-carbon ethylenic polymerization. Physical dispersion of one component in the other is also a possibility.

Varnish reactions are not as well known as alkyd resin chemistry. The former are difficult to measure whereas a variation in stoichiometric relationships of alkyd resin component controls and predicts the properties of the product.

In the early stages of the varnish-cooking process the oils serve as resin solvents. This property is directly related to their degree of unsaturation; tung oil is the best and unbodied soybean the poorest. When the "soft oils" are bodied, the trend is reversed. The solvency power increases from bodied soybean oil to bodied linseed oil.

The physical effect resins have on oils is related to their softening points. This varies with the degree of maleic anhydride and/or phenolic modification. The drop-method, softening point of varnish resins, as a class, varies about 90° to 170°C. as the modification, molecular complexity, and molecular weight of the resins increase. The effect of increasing resin molecular weight on oil and/or varnish viscosity is illustrated by the data in Table VI. In this case alkali-refined linseed oil and resin, in proportions for a 25-gal. varnish (2 parts oil and 1 part resin) were mixed and heated only to effect solution. The viscosity of these solutions increases with resin-softening point, thus indicating the immediate beneficial effects as related to the degree of resin modification and not oil carbon-to-carbon polymerization. If bodied oils are used in lieu of alkali-refined linseed oil, the effect is more pronounced. If the oil has a viscosity of 25 stokes and the resin a softening point of greater than 125°C., the oil/resin mixture is solid at room temperature.

TABLE VI
Relationship of Resin-Softening Point and Oil/Resin Solution Viscosity in 2/1 Ratio

Softening point of resin (°C.)	Viscosity oil/resin solution	
	Stokes	Gardner
90	3.7	O
112	6.0	T-U
135	16.8	X-Y
158	150.0	Z_6

Powers (22) has shown that variable amounts of oil and rosin will react to form a mixed rosin-fatty acid and glycerol ester and free fatty acids reaching an equilibrium with free rosin always present. Resins and oils also interchange. Powers verified this by cloud-point data. Montequi and Morales (23) used "mild" and "strenuous" saponification methods and concluded from their experiments that the interchange reaction did take place.

Most of the hard resins in use today are esterified with the aid of basic catalysts, such as zinc, lithium, lead, and calcium as their oxides, hydroxides, and organic salts. These convert to the resinates during the resin-cooking process. The same catalysts are also

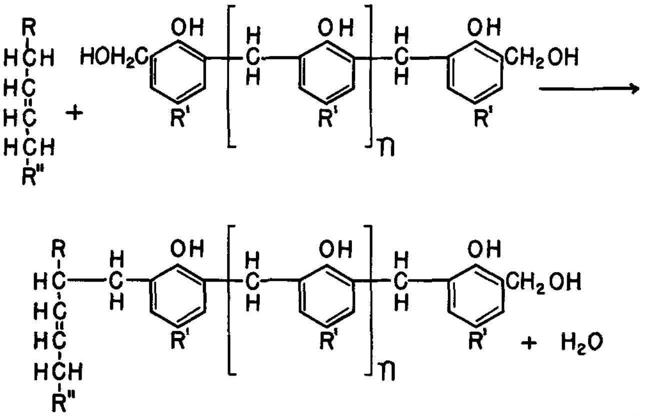

FIG. 5. Reaction of phenolic resins and oils, where R and R″ are other parts of the oil molecule.

used in the alcoholysis of oils, such as the reaction of oils and glycerol or pentaerythritol in the first steps in alkyd-resin synthesis. It is therefore very probable that these catalysts aid in an oil-resin interchange reaction, a much desired property in a varnish.

A varnish with a rosin ester is not likely to have a reaction between the oil and resin ethylenic groups to form a carbon-to-carbon linkage. It is possible that the fatty radicals do react at these groups to form homopolymers, as is evident from varnish-analysis data.

The chemistry of earlier varnishes which were based on "fused" or "run" natural resins was not understood; it was an art. In the light of what is known today, it may be possible to offer an explanation for this. Studies on these resins by Ruzicka and coworkers (24) indicated that, after running, or more correctly stated, depolymerizing these resins, they were composed of dibasic acids. These were in a measure no doubt responsible for the acidity which developed. Therefore it should be possible for these acids to interchange with the fatty acids in the oil. These resins always contain an ash residue, hence this may have been the necessary catalyst. On the basis of this reasoning the chemistry of the natural resin varnishes is not too far different from that postulated for rosin-based resins used today.

There is a wide variety of phenol formaldehyde resins with different properties. This is dependent upon the type and location of the substituent group or groups on the phenol, the ratios of phenol to formaldehyde, and the type of condensing catalyst. Consequently their reactivity with oils is different. Turkington and Allen (25) visualized that active hydrogen atoms probably on methylene carbon atoms, in oils, may react with a phenol alcohol about 230°C. to eliminate water, probably as shown in Figure 5. The substituent group on the phenol controls the reaction. Below 230°C. the water that is eliminated comes from the completion of the resin reaction. They based their conclusions on changes in specific refraction, viscosity, and gel characteristics. Powers (22) based his conclusions on cloud-point and solubility studies. Evidence also points to the fact that tung oil is more reactive than linseed oil.

The functionality of oil and resin and the oil/resin ratio are important in determining varnish properties. There must be a balance between the functionality of the component oils and resins as related to the degree and type of unsaturation in the former and the number of ester groups in both oil and resin. The latter, in turn, are a function of the number of hydroxyl and carboxyl groups, or the functionality of the polyol and resin-modifying acid. There does not appear to be any good relationship between unsaturation functionality of the fatty component and the hydroxyl functionality or carboxyl functionality if a polybasic acid is used, with an ultimate dried film characteristic as previously illustrated.

The literature in the area of oleoresinous systems in regard to the functionality concepts has not kept pace with the general technology of varnish improvements. This discussion is therefore limited by the lack of related reliable data.

Recent Advances

Recent years have not witnessed much progress in the area of hard varnish resins.

Soft Oil Varnishes. Since the hard resins preferably require bodied soft oils, it is advisable to prebody a large quantity and use an aliquot for each batch of varnish. A prebodied oil is necessary to preserve color. For certain manufacturing plants this is a disadvantage.

It was therefore apparent that the use of unbodied soft oils in varnish-cooking operations would possess definite advantages. A typical oil answering this description is soybean oil while the resin would of necessity require unusually high functionality.

Resins specifically designed for this use were patented in 1951 (26). This family of hard resins is based on rosin, and *alpha-beta* unsaturated dicarboxylic acids, usually maleic, a pentaerythritol, and catalyst. These resins differ from the resins, indicated in Table I, as being rosin adducts with unusually high percentages, namely 15 to 28% of *alpha-beta*

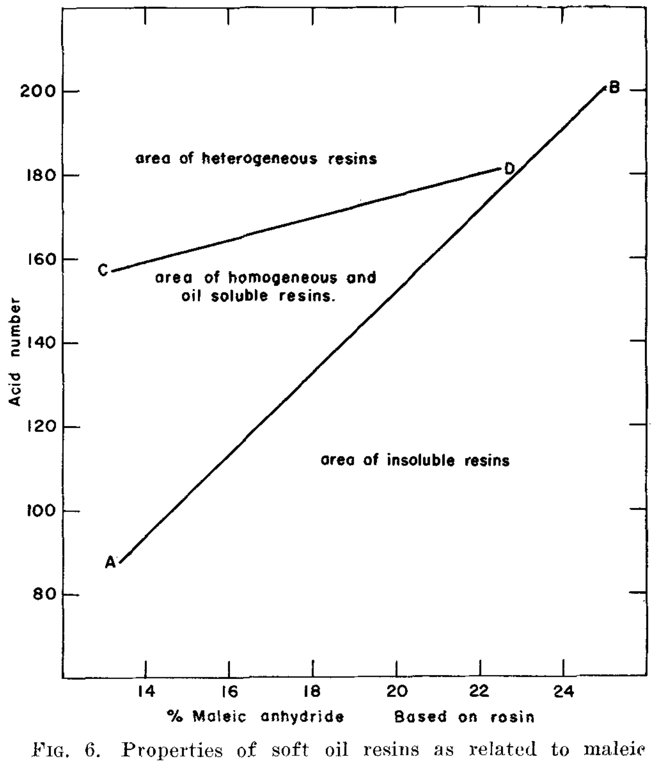

FIG. 6. Properties of soft oil resins as related to maleic anhydride content.

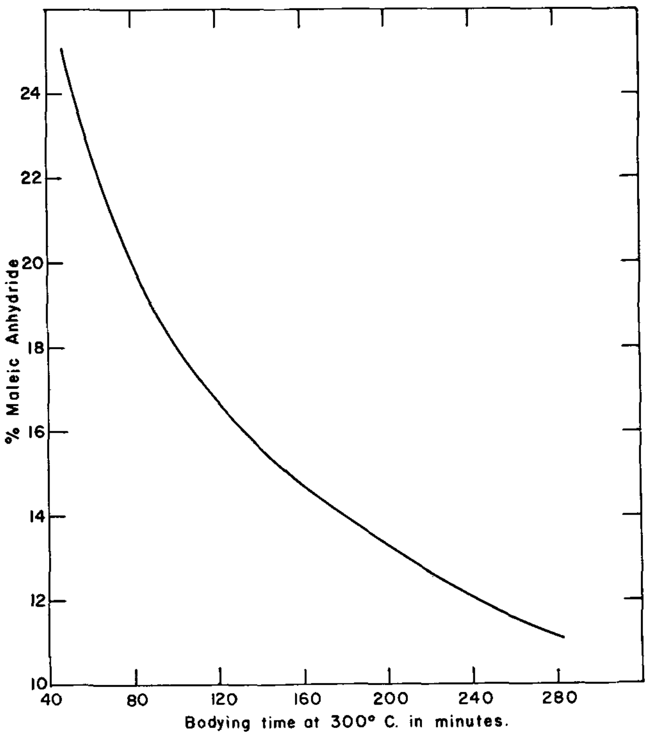

FIG. 7. Time required to read a "D" viscosity for 15-gal. soybean varnishes as related to maleic anhydride content.

ethylenic acids. On a molar basis this is 0.46 to 0.86 mole per mole of rosin acid. This determines their desirable properties. These resins have unusually high acid and hydroxyl numbers since the components are only sufficiently esterified to obtain clarity. The compositions of the resin and properties are shown in Figure 6. The space between the lines AB and CD, relating acid value and percentage of maleic anhydride modification, is the area of homogeneous and oil-soluble resins. If the acid value of these resins is taken below the line AB, they become oil-insoluble and in some instances infusible.

These resins contain unreacted hydroxyl groups in the range of 3.5 to 7.6%. The presence of free hydroxyl groups together with the basic catalyst makes ester-interchange reactions possible with the oils in varnish-cooking operations. This interchange reaction is important and may be entirely lost by gelation of the resin if too much oil, or an oil with a high viscosity, is used or if the acid value of the resin is too low.

The oil and resin interesterification reaction can be traced during the cooking process. These resins and soft oils are inherently incompatible below 240°C. in proportions for a 15-gal. varnish (55% oil). However after heating a few minutes, the melt clears. If longer oil-lengths are desired, more oil is added after reaching the clear point. The interesterification of oil and resin continues, resulting in varnishes of low acid value 10 or less with good colors.

The relationship between varnish-cooking time and the degree of maleic modification of the resin for a series of 15-gal. soybean oil varnishes to a viscosity of D at 50% nonvolatile in mineral spirits is shown in Figure 7 (26).

In this family of varnishes all the excess functionality is carried by the hard resin; the effect of oil ethylenic functionality is essentially negligible. Molecular size is obtained by forming a large cross-linked ester type of oil-resin molecules with little if any carbon-to-carbon polymerization. The oil functions as a built-in plasticizer for the high polymer resin moiety. Consequently the oil unsaturation is reserved for film drying, oxidation, and conversion from the liquid-to-solid phase. This is most desirable.

At this point, these questions remain unanswered.

Can identical varnishes be prepared by using a highly modified oil with a resin with little or no modification, and an unmodified oil with a highly modified resin?

Is there a mathematical relationship between varnish properties and the total modification found in both oil and resin?

Does a high modification in the resin have a greater effect on an equal weight basis than the corresponding modification in the oil, or *vice versa*?

These questions immediately suggest a research problem which might lead the varnish maker to correlate facts with numbers.

Hard Oil Varnishes. The resin requirements for hard oils are different from those of soft oils. Unless properly processed with the correct resins, hard oils dry to wrinkled and frosted films in air containing products of gas combustion and nitrous oxide. This is known as "gas checking," or the varnish is said to be "not gas-proof." This is an external condition which influences the drying of the film; no gas or other products are evolved from the film at this stage of the drying process.

The term "gas-proof" originated during the days of the tung oil baking varnishes and enamels. The ovens used in the baking operations were quite crude and were heated with open natural gas burners frequently without flues. The finishes to be baked were placed in the space above the burners; the air contained the products of combustion. In some ovens the conditions were more severe than in others, consequently a coating might perform in a satisfactory manner for one finisher and fail miserably for another. This led to the development of certain tests for determining gas-proofness. Tung varnishes and enamels which passed these tests failed under actual operating conditions.

To gas-proof it, tung oil must be heated rapidly to about 560°F., held for several minutes, and chilled rapidly. This technique is known as "thermolizing" and is covered by a number of patents (27). These processes have now become obsolete because of the small volume of tung oil requirements.

Cheap tung oil varnishes were usually made with ester gum as the only resin. For most purposes these varnishes performed well, but under the above conditions they were not completely gas-proof. The use of modified (nonreactive type) phenolic resins improved the gas-proofness, but, again unless conditions were very closely controlled, the gelation tendency was not eliminated.

Varnish makers were aware that the degree of gas-proofness of a tung oil varnish was a function of the temperature to which the oil was heated, the length of the time held at a given temperature, and the type of resin. They did not know what actually was taking place in the oil during this process but were aware that a phenolic resin was desirable.

Obviously two things were needed, namely, a method for testing the gas-proofing efficiency comparable to the most severe operating conditions; and a study of the changes in tung oil to effect gas-proofness. An

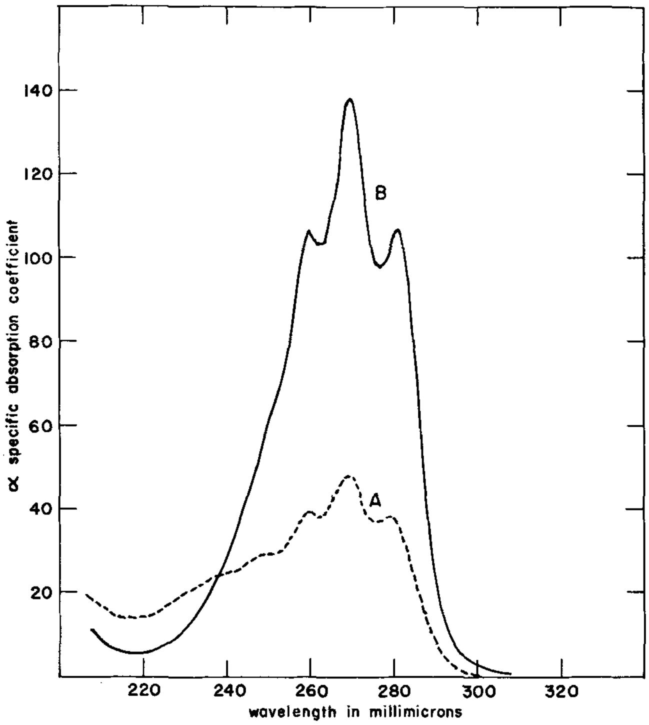

FIG. 8. Specific absorption coefficients of raw and heated tung oil: A—tung oil heated to 305°C. and chilled instantly; B—raw tung oil.

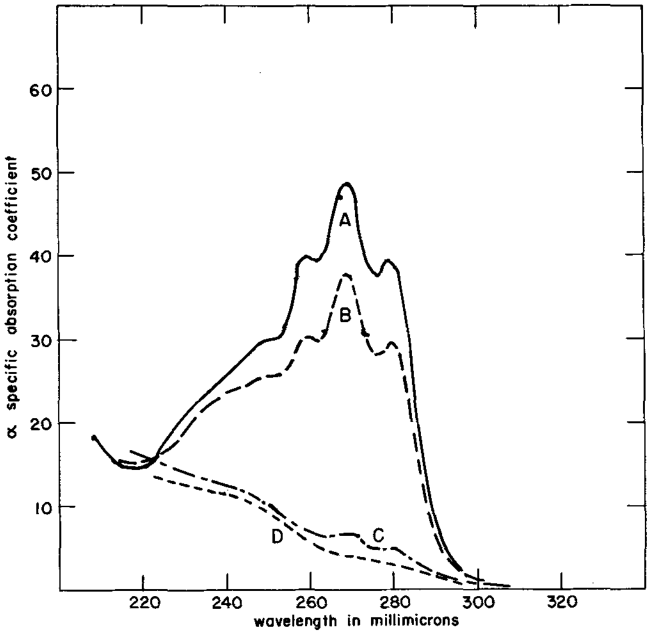

FIG. 9. Effect of heating a 25-gal. tung oil pentaerythritol rosin ester varnish and degree of gas-proofing: A—heated tung oil; B—varnish heated to 305°C.; C—varnish held 10 min. at 305°C.; D—varnish held 25 min. at 305°C.

ideal resin for this use was one which would completely gas-proof the oil at a low temperature and at a rate such that bodying of tung oil could be controlled.

Some qualitative results reported by Oswald (28) indicated that there was a relationship between the disappearance of the conjugated triene structure and gas-proofness. This was measured by the ultraviolet absorption characteristics between the wavelengths of 220 and 320 millimicrons for raw tung oil, treated tung oil, and tung oil resin combinations. These results are shown in Figures 8, 9, and 10.

Curve B of Figure 8 shows the typical triple peaks at 268 millimicrons for triply conjugated ethylenic bonds of tung oil. Curve A of the same figure shows the characteristics of the same oil heated to 305°C. in 18 min. and chilled instantly. The height of the peak in Curve A is 34% of that of Curve B, or since the tung oil contained 80% of the triply conjugated eleostearic acid, about 27% of the oil remained in the triply conjugated form.

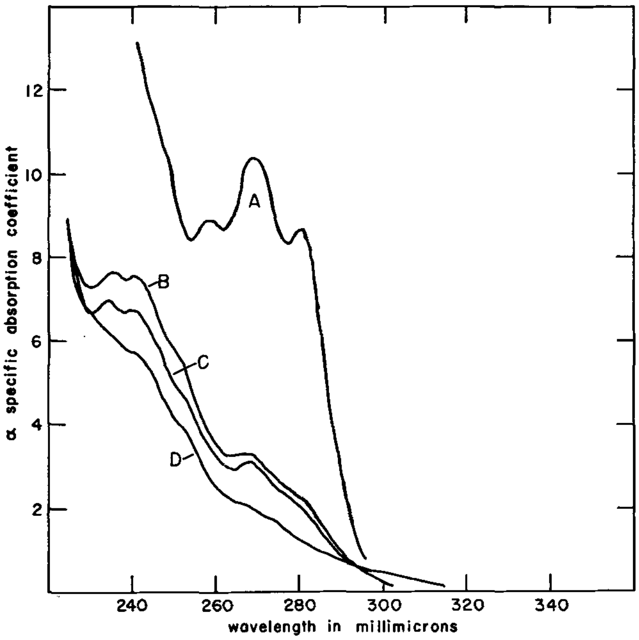

FIG. 10. Effect of various resins on gas-proofing of varnishes: A—phenolic resin; B—ester gum; C—rosin pentaerythritol resin; D—phenolic- and maleic-modified rosin esters.

The curves B, C, D of Figure 9 were obtained by heating the same tung oil with a rosin-pentaerythritol resin in 25-gal. proportions to 305°C. and holding 10 and 25 min. at 305°C., respectively. Curve A is the same as Curve A of Figure 8 and serves as the control. By applying the same calculations as in Figure 8, the three varnish samples show 35%, 5%, and essentially no triene, respectively. The varnish of Curve D showed no gas-checking by the more severe method described by Oswald (28).

With this resin it is obvious that the time of heating governs the degree of varnish gas-proofness as related to the residual triene content.

Figure 10 shows the effect of various resins and the residual triene structure as related to gas-proofness. Curve A shows the triene content of a 25-gal. varnish in which the phenolic resin was designed specifically for use with tung oil; this was gas-proof at 7.5% triene. Curves B, C, and D are for varnishes containing 20 gallons of tung oil and 5 gallons of linseed oil. Curves B and C are for a rosin pentaerythritol resin and ester gum, respectively, and will gas-proof at 1.5% residual triene. Curve D is for a maleic-modified pentaerythritol resin ester and phenolic resin. From these curves it appears that the degree of gas-proofness varies with the nature of the resin. This is related to recent work by Goldblatt, Hopper, and Rayner (29) on the preparation of tung oil alkyd resins and indicates that 8% triene residue produces a gas-proof resin. This is in agreement with some of the previous data.

As the triene structure disappears, a six-membered ring is formed by the addition of two fatty chains probably as shown in Figure 11. Isomers are possible. These do not show the addition of phenolic resin which may be analogous to that indicated in Figure 5. Obviously, if the structure of Figure 11 is the result, there is sufficient unsaturation remaining for oxidation and further polymerization.

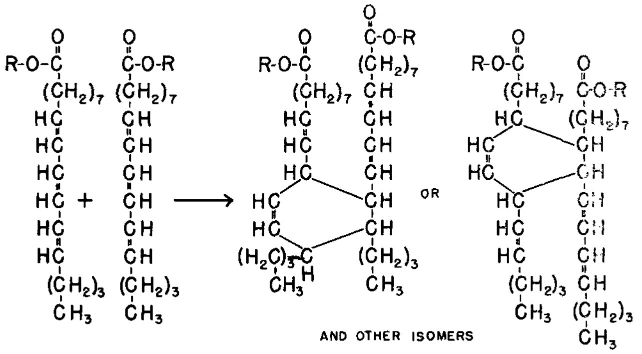

FIG. 11. Disappearance of triene in tung oil with formation of various isomers; R is the remaining part of glyceride molecule.

All of the varnish resins discussed up to this time required heating to produce varnishes. It is generally felt that cold-cut blends of resins and oils usually yielded products which are inferior to the cooked products. However Breslow (30) claims that a varnish superior to the cooked type results when a pentaerythritol ester of a dehydro-abietyl-N-substituted carbamic acid is used.

Richardson (31) described an exception to the necessity of heating tung oil to obtain gas-proofness. A cold cut of a phenolic resin in xylene and isopropyl alcohol, BR 9400, proved effective with tung oil.

In Situ Processes

The varnish maker has a more definite control over his varnish components in the *in situ* process. The *in situ* methods for cooking varnishes vary from simple to complex. The simplest is the preparation of a mixed ester or rosin and drying oil fatty acids, with either glycerol or a pentaerythritol as described in 1937 by Rheineck, Rabin, and Long (32). This has been translated in recent times to mean the use of tall oil. In 1956 146 million pounds of tall oil were produced, divided between *in situ* varnishes and alkyd resins. Further modifications include the use of *alpha-beta* ethylenic carboxylic acid with a pentaerythritol.

An important item in *in situ* varnishes is the polyol. Tess and May (33) conducted a study of the effect of polyol variation on tall oil coatings in 1950. They concluded that pentaerythritol esters were the more stable at high temperatures. This stability is now an accepted fact. Recently Vaughan (34) explained the stability of the neopentyl structure on the basis of electronic concepts.

Various modifications of combining monomer fatty acids and resin acids prior to *in situ* cooking operations are found in the literature. Scott (35) claims that co-reacting rosin, fatty acids, and maleic anhydride, followed by the addition of polyhydric alcohol, yields a better varnish than when the maleic anhydride is reacted with either monobasic acid first.

Conclusions

It seems quite apparent that the use of drying oils in classical varnishes is giving way to the use of oils in similarly functioning coatings or drying oil-free coatings.

The chemistry of drying oils in the varnish-cooking process is not too clearly established but appears to be one of ester interchange between oil and resin. More research in this area is indicated. However if future research is to be undertaken, it must be justified. In view of the declining varnish market, this is doubtful.

Lack of data makes it impossible accurately to correlate oil and resin functionality into a usable mathematical relationship.

Acknowledgment

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REFERENCES

1. Barry, T. H., Drummond, A. A., and Morrell, R. S., "The Chemistry of Natural and Synthetic Resins," D. Van Nostrand and Company, New York, 1926.
2. Mattiello, J. J., "Protective and Decorative Coatings," vol. I, ch. 1, John Wiley and Sons, New York, 1941.
3. Modern Varnish Technology, Hercules Powder Company, 1957.
4. Tariff Commission Reports, Synthetic Organic Chemicals, United States Production and Sales, 1941 to 1957, inclusive.
5. The Fats and Oils Situation, May 1959, Agricultural Marketing Service, United States Department of Agriculture.
6. a) Naval Stores Statistics, 1900–1954, Statistical Bulletin No. 181, United States Department of Agriculture, Crop Reporting Board, June 1956; b) Agricultural Statistics, United States Department of Agriculture, 1957 and 1958.
7. Renfrew, M. M., Schroeder, H. M., Hauge, H. M., and Waythomas, D. J., J. Am. Oil Chemists' Soc., *35*, 19 (1958).
8. Stanton, J. M., A.O.C.S. Drying Oils Symposium, Minneapolis, Minn., August 1959.
9. Findley, T. W., New Coatings and Coatings Raw Materials Symposium, North Dakota Agricultural College, Fargo, N. D., June 1959.
10. Greenlee, S. O., New Coatings and Coatings Raw Materials Symposium, North Dakota Agricultural College, Fargo, N. D., June 1959.
11. Kittle, H., Deutsche Farben. Z., *10*, 16 (1956).
12. Pollini, A. P., Ind. della Vernice, *3*, 146 (1949); BPV *23*, 32 (1950).
13. Letts, P. A., BPV, *23*, 32 (1950).
14. Rheineck, A. E., Devoe and Raynolds Company Inc., U. S. 2,192,152 (1940).
15. Holman, R. T., Lundberg, W. O., and Malkin, T., "Progress in the Chemistry of Fats and Other Lipids," ch. V, Pergamon Press, London, 1958.
16. Wilson, R., J. Oil Col. Chem. Soc., *33*, 503 (1950).
17. Clocker, E. T., U. S. 2,188,882,-3,-4,-5,-6,-7,-8,-9,-90 (1940).
18. Ullman, H. M., Small, J. G., and Artim, E., U. S. 2,587,411 (1952).
19. Rheineck, A. E., J. Am. Oil Chemists' Soc., *28*, 456 (1951).
20. Greenlee, S. O., Devoe and Raynolds Company Inc., U. S. 2,345,408 (1949).
21. Tess, R. W., and May, C. A., Off. Digest, No. 311, 1145 (1950).
22. Powers, P. O., Ind. Eng. Chem., *42*, 146 (1950).
23. Montequi, R., and Morales, J. P., C. A. *47*, 4629 (1953); C. A. 45, 7317 (1954); C. A. 49, 640 (1955).
24. Ruzicka, L., Steiger, R., and Schinz, H., Helv. Chim. Acta, *9*, 962 (1926).
25. Turkington, V. H., and Allen, J. Jr., Ind. Eng. Chem, *33*, 969 (1941).
26. Rheineck, A. E., Hercules Powder Company, U. S. 2,569,495 (1951).
27. Mattiello, J. J., "Protective and Decorative Coatings," vol. III, ch. 2, John Wiley and Sons, New York, 1943.
28. Oswald, F. J., Off. Digest, *308*, 667 (1950).
29. Goldblatt, L. A., Hopper, L. L. Jr., and Rayner, E. T., Am. Pt. J., *43*, 81 (1959).
30. Breslow, D. S., Hercules Powder Company, U. S. 2,575,290 (1950).
31. Richardson, S. H., Paint, Varnish Prod., *45*, 9, 25 (1955).
32. Rheineck, A. E., Rabin, B., and Long, J. S., Devoe and Raynolds Company Inc., U. S. 2,077,371 (1937).
33. Tess, R. W., and May, C. A., Off. Digest, No. 311, 1145 (1950).
34. Vaughan, C. L. P., New Coatings and Raw Materials Symposium, North Dakota Agricultural College, Fargo, N. D., June 1959.
35. Scott, L. K., Devoe and Raynolds Company Inc., U. S. 2,427,327 (1947).