

·

)

UNITED STATES DEPARTMENT OF AGRICULTURE AGRICULTURAL RESEARCH ADMINISTRATION BUREAU OF AGRICULTURAL AND INDUSTRIAL CHEMISTRY

ABSTRACT EIBLIOGRAPHY OF THE CHEMISTRY AND TECHNOLOGY OF TUNG PRODUCTS, 1875 - 1950

1

Compiled by

Ralph W. Planck and Frank C. Pack Southern Regional Research Laboratory

and

Dorothy B. Skau

New Orleans Branch United States Department of Agriculture Library

VOLUME II

4

2

.

SOUTHERN REGIONAL RESEARCH LABORATORY 2100 ROBERT E. LEE BOULEVARD NEW ORLEANS 19, LOUISIANA

, 7

.

•

(e) Drying and Film Formation

Albrecht, H.

THE TUNG OIL PHENOMENON AND THE DRYING OF OILS BY IONIZED OXIGEN. Farben-Ztg. 39, 15-16 (1934): C.A. 28, 1877 (1934). "Using a limed rosin-tung oil varnish, A. was unable to confirm Rossmann's observations (cf. C.A. 27, 5557). The wrinkling of tung cil films is ascribed to the presence of N oxides whose formation in turn may be due to active gases.

e.g. Og or other exidizing gases." From C.A.

Auer, L.

THE CRUSTALLIZATION OF WOOD OIL FILMS. Farben-Ztg. 31, 1625-7 (1926): C.A. 20, 2418 (1926).

"Various theories concerning the nature of the opaque drying of wood oil films are reviewed. It is not due to crystals of beta-eleostearin but is caused by micro- and macroscopic wrinkling. The drying of wood cil was studied under different degrees of humidity in white plass desiccators. Films allowed to dry in the room, and showing wrinkling became clear when placed in a moist atm. in a desiccator. Films dried over CaCl, were also clear. The evolution of HoO during the drving of wood oil is readily shown by incorporating anhyd. CuSO4 in the film. The salt turns blue during the drying. Ultra-violet light is the deta. factor in the film wrinkling, not the adsorption or evolution of moisture. The films dried clear in the desiccators because of the absorption of the ultraviolet in the thick white glass. The same effect occurs in Pb vessels irrespective of moisture content. Ordinary window class does not absorb enough of the ultraviolet to stop the wrinkling." From C.A.

Auer, L.

MOM-LIQUID DISPERSE SYSTEMS OF THE FATTY (ILS. Kolloid-Z. 42, 288-92 (1927); C. A. 21, 3789 (1927).

"Film formation of fat oils is not an oxidation in a true chem, sense but depends on the gas conen. in the oil. A careful examples the sense of wood oil, linseed cil and sunflower oil as to surface tension, H-ion conen., microscopie example, contribuging and I no. The gal and sel conditions of these colloidal materials are very important in their drving properties." From C.A.

Auer, L.

COLLOIDAL CHANGES IN FATTY CILS. Netl. Paint Bull. 1, 8-8, 18 (June, 1937); 8-11 (July, 1937); C.A. 31, 7268 (1937).

"Erptl. data on the drying of linseed oil, boiled linseed oil, linseed oil fatty acids, sunflower oil with red lead, tung oil with red lead and poppyseed oil with red lead under different conditions of atm. and pressure.****". From C. A. Auer, L.

THE ACTION OF ALTER ON THE DRYING PROJESS OF FATTY OILS. I and II. Paint Varnish Production Mar. <u>17</u>, 12-4, 16-8 (Nov. 1937); 12-4, 16-8 (Dec. 1937)*: C.A. 32, 3168 (1933).

"I. The degree curves (increase of weight against time) for Il different eils (6 linseed, tung, poppyseed, sunflower, walnut and linseed oil fat acids) and 6 rod lead paints were studied in the lab. and in desiccators with varying vapor pressures of water. Swelling isotherms are also obtained, where increase of weight over a certain which after equil. has been obtained is plotted actingt waper pressure. Both sets of curves are quite erratic, but some of the swelling isother's show the expected S-shape.

II. Adul. strids are given in which already dry films were used, one in which the desiccators contained air as well as where v per, one in which CO_2 replaced the air, and one in which no gas other than water was present. The Veror curves for these expts, were more consistent, and the swelling isotherm apprached pere glosely to the expected S-shape." From C.A.

Bultimore Paint & Varnish Production Club

OITICICA OIL. POSSIBLE SUBSTITUTE FOR WOOD OIL. P.int Oil Dhem. Rev. 27 (23), 66-3 (193E); Cil Paint Drug Reptr. 128. (22), 53 (1935)*; C.1. 30, 4689 (1936).

"The possibility of producing large ants. of citicles cil (I) is fiscussed. Results obtained when using the oil to replace varying propertiens of the tung oil is a 35-gal. ester-tung oil sper, moeting the requirements of Federal Specification TT-V-121, are reported. The straight I varnishes were slightly inferior in regard to resistance to water and NaOH: inferiority in closs retention, checking and general appearance was revealed by a 12-week exposure test made at Richmond, Ja., beginning June 7, 1935. Replacement of only 1/3 of the tung oil gave films of comparable quality except as regards luster. Such varnishes dried satisfactorily with a standard Pb-Co drior mixt. (0.97% Pb-0.022% Co). If 1/2 or all the tung oil was roplaced by I, an increase in Co or the use of Co and Mn driors was required. A Mn-Fb drier mixt. was unsatisfactory for such varnishes. Varnishes mede from I, liquefied under optimum conditions (435°F. for 30 min.). did not differ from those made from rew oil except that the former required less time to reach the end point in the varnish kettle. Since the substitution of I for tung oil lengthens the reaction time in the kettle, the cooking procedure will have to be varied for best results." From C.A.

Bauer, K. H. and Gonser, K.

THE PERHABILITY OF FILMS OF DRYING OILS. Chem. Umschau Fotte, Oele, Nachseu.Harz 31, 197-9 (1924); C.A. 18, 3729 (1924).

"To test oil films for their permeability by aq. solns. B. and G. satd. silk bolting cloth with the oil to be tested. removed the excess by drawing the clamped gauge between 2 class rods and then dried the films, protected from dust and sunlight and clamped in a special Al frome which bermitted weighing. After 2 or 3 mos. a perfectly dry film had formed that carried 0.0036 - 0.0050 g. linsed oil per sq. cm. By corefully clomping such films air-tight between 2 tubulated glass 'ulf spheres, one of which was filled with distd. H20 or some reagent and the other with a crystalloidal or colloidal soln, any diffusion could then be observed by the color in one or both half spheres: Linseed, perills and Chinese wood oil films showed diffusion of Cl, Fe and CNS ions in 2-8 days but colloidal Au soln. would not diffuse, while a 3-mos.-old film of he wild boiled oil, corrying 0.0779 g. per sq. cm., showed ne diffusion whatever. Diffusion through cracks or nonimpregnated silk meshes was excluded. Expts. not yet complete with NHz, HoS and CO, indicate a rapid diffusion of these gases through the films." From C. L.

Beyer, R.

WHAT IS TUNG OIL? Tung World 3 (12), 6-7 (Apr., 1949).

A brief review of tung oil, written in 1931, covering its source, draing properties and ese in protective coatings, improgramts, rubber extenders, etc.

Blon, A. V.

THE MECHANISM IN THE FORMATION OF WRINKLES IN WOOD OIL FILMS. Chem. Umschau Fette, Oele, achiseu, Harze 36, 229-36 (1929); C.A. 23, 5336 (1929).

"The formation of wrinkles may occur simultaneously with that of crystals of beta-eleostearin; either formation may occur suparatoly, and crystn, may appear before or after wrinkling; no definite law could be formulated to correlate these variations. The change of alpha-eleostearin to the cryst. beta-form seems to be bound up with light rays of long wave longth. The growth of mols. into larger complexes by condensation or polymerization, etc., causes formation of "gern" nuclei which are less sol., offor less active surface and have a tendency to travel toward the surface where their increasing no. finally push the solvent way and form a continuous layer, the individual mols. of which are standing upright with the surface potential at a min. Solid monomol. films possess no surface tonsion, verified by tests with wood oil films under the microscope. A desolvation implies a vol. increase, resulting in wrinkles. The film during aging is

subject to internal stresses which show themselves by double refraction with crossed nicels." From C.A.

Carrick, L. L., Knudson, G.E., Porter, J. V., and Thompson, H. J.

DRYING OF VEGETABLE OILS.

Amer. Print J 23, (30), 58-62; (32), 18-21, 56-60; (34), 54-60; (36), 14-18; (38), 21-24; (40), 16-21, 44-45; (43), 45-50; (45), 16-18, 43-45; (47), 46-51; (49), 16-22; 53-58 (1938); 24, (3), 53-58; (5), 54-60 (1939)*. Brit. Chem. Abstracts 1940, B, 221.

"The changes occurring during the drving of oil films have been studied by determinations of the composition and chemical consts. of the film. Pb and Co drivers are found to accelerate the changes without influencing the nature of the final product. In the chase of raw perilla and linseed cils the O. absorption excouls that required for peroxide formation at all the ethylenic linkings and some oxidative splitting with formation of COoH groups occurs. With raw tung oil 02 addition occurs rapidly at two of the ethylenic linkings of the elaeostearic group. The middle double linking of the conjugated system is not the first to be attacked, since a conjugated system is still present after onough 0, has been absorbed to saturate one ethylenic linking. Oxidation at the third ethylenic linking results in the formation of acids and volatile and COMe2-sol. products. With safflower oil the initial increase in wt. is followed by a fearons due to the exidative splitting, forming volatile oreducts." From Brit. Chem. Abstracts.

Chatfield, H. W.

HOW TO OVERCOUP DEFECTS OF FILMS AND FILM-FORMING COMPOSITIONS. Paint Manuf. 8, 19-21, 56-8(1938); C.A. 32, 3175 (1938).

"These installments deal with the following properties: flow-gelation--snottiness, greenness, lifting of undercoats, livering--fattening--feeding--stoutening--gelling--skinning, spotting, sweating--comeback, webbing, alligatoring, crocodiling, erow's footing--crystg., frosting, gas checking, wrinkling-swelling--shrivelling." From C.A.

To sure of these defects tung oil films are susceptible.

Cloveland Paint & Vernish Production Club

HUMIDITY AND TEMPER TURE EFFECTS ON PROTECTIVE COATINGS. II. DRV DNG OF OILS. Natl. Paint, Varnish Lacquer Assoc.Circ.629, 315-18 (1941); C.A. 36, 2432 (1942).

Plate-plass panels were conted by means of a steel draw-blade with linseed oil, dehydrated castor oil, heat-bodied, alkalirefined linseed oil, heat-bodied, blown, stabilized linseed oil, blown linseed oil, blown soybean oil, heat-bodied soybean oil, thermolized tune cil, heat-bodied, blown fish fil, heat-bodied fish eil and heavy, blown fish eil, resp., contg. Pb-Ma-Co, Pb-Co and Pb-Ma krier combinations and dried in a special app. et 50°, 77° and 95° at 35, 65, and 95% relative humidity with the following results: (1) Grying differences lue to differences in humidity and temp. are not much affected by drier conc. provided at least the usual min. quantities are used; (2) drying is slower at higher umidity and temp. than at intermediate humidity and temp; (3) retartation of drying by excess drier is more pronounced with heat-bodied than with blown ofls; (4) blown foils are less sensitive to humidity effects than straight heat-bodied cils; and (5) dehydrated caster oil, as well as tung oil, shows only meterate susceptibility to high humidity in comparison to the 4 tuppe of linsped oil." From C.A.

Damenberg, H., Dagars, J. K., and Bradley, T.F.

FROSTING AND GAS-CHECKING OF COMJUNITED DRVING OILS. Int. Bin.Chom. 42, 1594-9 (1980); C.A. 44, 9160 (1950).

"The tendency of drains oils and resins conts. fatty acid radicals of conjugated unsate, structure to under to "frosting" or "checking" during their drying and film formation has been subjected to new expile investigations in an attempt to reach better understanding of this phenomenon, its cause, and means of correction. This affect has been found to be greatly influenced by atm. dust contamination. Find dust particles, such as fibers or soot which may coour in the atm. and settle on the drying films, are similiont factors tending to induce frasting and "gas-checking." The sort concrated by the kerosene lamp of the commonly employed ras-checkin; tester appears to have a similar effect. Small ants. of certain surface-active aronts, such as calcium octoate and the colleium sults of phenolic resins, control fresting and checking. Nevertheless, it is recommended that the industry denote particular attention to the removal or minimization of Just contemination in the atm. in which coating compns. are applied and dried." From C. ...

Eibner, A.

THE DRING OF FITTY CILS.

Forben-Ztr. 30, 3055-6 (1925); Ferbe u. Lock 1925; 457; C.4. 20, 117 (1926).

A review of the mechanism of the drains of cils with special attention to Chinese wood cil, linseet cil and poppy-seed cil.

Eibner, A.

AUER'S CONCEPTION OF THE DRYING OF OILS. Farbon-Ztg. 33, 2165-9 (1928); C.A. 23, 1291 (1929).

"The 'gas congulation' theory is 'criticized mainly on the grounds that in its evolution Auer has ignored the work of earlier investigators on the individual charactoristics of various dils,

				A CONTRACT OF
	hydrophilic nature			
	nuther's expts. in	this fiel have	briefly reca	pitulated."
11 TU - TU	O'ente		•	· • •
		·		
	lthough attention i		fly.on linss	ad oil the
°r,/13	ag of tung oil is a	lso mentioned.		
	*			
Eibner, A.				
TUE .	PRESENT POSITION AS	REGARDS THE IN	WESTIGATION (OF THE FATTY
DRIT	NG OILS.			
Pain	t Varnish Productic	n Mgr. <u>33</u> , 4,6,	8-10 (July, 1	1929).
ري. الله	booming of sil darri	na from the tim	ດ ດີ ຟັນປີດ້ານກ	(1867) + 0

Theories of oil drying from the time of Mulder (1867) to 1929 are critically reviewed. China wood cil, alpha-eleostearic acid and bota-eleostearic acid are mentioned briefly in examples.

Eibner, A.

THE VELLOVING OF OIL FILMS AND I IS TREVENTION. -Point Varnish Production Mar. 40, 12,14,30-1 (Mar., 1936).

Films of dried linseed cil all of dried wood oil reveal differences in degree and in kind of yell wind when examined by ultraviolet light. These results do not prove the existance in the oil molecule of keto groups adjacent to etheroid double linkages.

Eibner, A., and Munzort, H.

OXYNS. V. OLL FILES CONSIDERED COLLOID-CHEMICALLY. Chem. Umschau Fette, Oele, Wachse u. Harze 34, 183-9, 208-11 (1927)*; C.A. 21, 3753 (1927).

"in exam. of various 6 months! old oil films and of their drying cils is discussed with tables of analysis.

Boiled

		Linseed oil	linseed		oil		linseed	cle- l .stearic acid film
I no.		173.5						
Acid no.	3.3	2.3						
Sapon. n.	193.3	191.5		•				
Hexabromide								
no.		50.7			•			
% insel. in								
ether and					• •			
alc.				60	85	36	64.5	7 6
% srl. in								
ether and				1.0	•	C A		0.4
alc.				40	14	64	35.5	24
% s: 1. in		,		0 5	2.0	4	7 5	(acotone)
het H ₂ 0 % scl. in				6.0	-2 · U	·±	0.0	(ado cone)
				10.5	8.0	10	8.0	
ether % sol. in				TOPD	0.0	10	0.0	
% SOL. IN alc.				27	1.0	50	24.0	
alc.				Ŵľ	14 O	50 _* , .	4'± €U	

The ether-sol. pertion of the films consisted largely of satd. fatty acids, while the alc.-sol. pertion contd. mostly hydroxy-glycerides. Kept in a closed bettle a linseed-oil film became a brown sirup in 2 yrs.; beiled linseed oil films and beiled wood eil films remained essentially unchanged after 7 yrs. The % of sol. and insel. portions in young dry films is tabulated:

		07	%	% insol.
Film ·	Drying time	sol.	insol.	after 6 months
Fresh wood oil	1-1/2 days	85	15	60
Tokyel	1-2 hrs.	83	17	86
Fresh linseel cil	7 days	72	28	36
Boiled linseed oil	12 days	50	50	64

These films are solid solns., formed by a flocculation reaction; the amt. and nature of the gels wary with the cil and the sols are glycerides of beta-elecstearic acid (in wood oil) and alphaand beta-linelic acid (in linseed oil). Moed al dries more rapidly at low 0, absorption because it colatinizes more readily than linsoed bil and keeps absorbing 02 through its surface up to a 14% increase in wt., followed by no essential decrease. Linseed oil gelatinizes less readily and dries therefore at max. oil absorption (17.5%) and a tecrease in wt. follows. Analysis of the wood wil film exts: (1) H_20 ext. acid no. 453.83. (2) Alc. oxt. acid no. 123.74, sapon. no. 205.9, ester no. 82.2, I no. 3.68. (3) Ether ext. acid no. 90.13, sapon no. 203.37, ester ab. 113.3, I no. 2.00. A wood bil film, 6 months; eld, was placed in a closed jor where it developed a sharp acid ador after a few weeks and became sticky. Microscopic, ultramicroscopic and Runtgen ray examn. should be practiced more extensively in connection with paint films." From C.A.

Eibner, A. and Rossmann, E.

CHINESE WOOD OIL IV. WOOD OIL AS A CRYSTALLOID. THE AUTOXY-POLYMERIZATION DURING DRYING. Chem. Umschau Fette, Osle, Wachse u. Harze <u>35</u>, 241-50 (1928)*; C.A. 23, 291 (1929).

"Sunlight and ultra-violet light chonge part of the alphaeleostearin, the principal constituent of Chinese wood cil, rapidly into the cryst. beta-eleostearin, n. 61°; dispersed devlight changes it slewly and no change or a very slow change occurs in the dark. These beta- crystals can be seen under the microscope in polarized light at 0°, but at room temp. the crystals re-dissolve in the cil up to 107. The change from the alpha to the beta form is the first step in the drying process of Chinese wood vil. The next step is in the conversion of the crystals into a film under the influence of light, heat and O2. The opt. conditions for rapid drying are: intense light (sunlight), high temp. (70°) and presence of 02. The crystals absorb 02 up to 12%, become insol., disperse, de not melt, and their acids have mol. wts. of 380-900 indicating polymerization. The polymerized insta product forms with the still unchanged oil an apprently finished film, and its final unexplored phase is the gradual filming of alpha-eleostearin." From C.L.

Eibner, A., and Rossmann, E.

CHINESE WOOD OIL. V. CRAZING AND FOLDING DURING DRWING. Chem. Umschau, Fette, Oele, Wachse u. Harze 35, 281-90 (1929)*: C.A. 23, 1516 (1929).

"Microscopic exam. of exptl. films on class of Chinese wood oil revealed a shrinkage in vol. and the formation of fine cracks while the film was still moist, the cracks reaching through to the bottom. This contraction coincides with the formation of beta-eleostearin from the alpha-variety by polymerization or condensation. The next step in drving is the formation of folds at right angles to the cracks, increasing the vol. and frequently pushing the cracks together again to form a double-lipped joint; this folding coincides with the absorption of 02 by alpha-eleostearin. Opposed to this view are the facts that beta-eleostearin alone, when melted, will show contraction and crack formation, and also that the drving curves of beta-eleostearin indicate primary oxidation, followed by polymerization. Drying the films in the dark always prevents wrinkling and clear films are obtained. In the light of the quartz lamp wood oil never dries clear; in sunlight at lower temp. simple wrinkling occurs without crackinr; alpha-eleostearin does not appear to cause cracking at room temp. It has also been observed in a black wood oil varnish that a network of fine cracks can form after the wrinkles appeared, passing through the wrinkles at all angles." From C.A.

Eibner, A., and Rossmann, E.

CHINESE WOOD OIL. VI.

Chem. Umschau Fette, Oele, Wachseu-Harze 37, 65-71(1930)*; C.A. 24, 2620 (1930).

"The microscopic "cracks" which had been noticed by E. in Chinese word oil films just prior to wrinkling during drying are now recomized to be microscopic deep foldings, representing the first stage of wrinkling. Beta-eleostearin consists of crystals formed from alpha-eleostearin by isomerism under the influence of sun or ultra-violet light, the latter causing crystn. in half the time required by sunlight. Double refraction has been observed in wrinkled films of wood, linseed and poppy-seed oils; in old films this becomes visible only with strong illumination at 300." From C.A.

Eisenschiml, Otto

PERILLA OIL, CENTER OF INTEREST, IS ASSUMING LEADERSHIP BASED ON ITS SPECIAL FRATURES.

Am. Paint J. 20, 16, 18 (Oct. 14, 1935)*; C.A. 30, 306 (1936).

"Perilla eil has definite properties differing from those of linseed oil. It bodies more quickly than linseed eil and has to be watched more carefully but is not nearly as delicate a product as China wood oil. It works well with synthetic resins but does not yield as waterproof or as hard a film as China wood oil." From C.A. Fahrion, W.

FATTY OILS IN THE LIGHT OF MESOMORPHOUS POLYMERIZATION. Ber. 49, 1194-6 (1916); J. Chem. Soc. 110, A, I, 628 (1916); Chem. Zentr. 1916, II, 37.

"The author has frequently criticized Eronstein's views (see Farben-Zeit., 1912, 1913), and now attacks his last paper severely. It is asserted that the different drying capacities of oils must be due first and foremost to their chemical constitutions. Particularly wood oil owes its unique properties to the fact that it largely contains alpha-eleostearic acid, and castor oil to its ricinoleic acid, which are peculiar to these oils." From J. Chem. Soc.

Farmer, C.S.

THE VELONING OF PAINTS. Paint Manuf. 5, 382-3 (1935); C.A. 30, 1594 (1936).

Nood oil causes more yellowing than other drying oils. Perilla and linseed are next while soybean oil, poppyseed oil and sunflowerseed oils cause the least. High acid values in oils increase yellowing. Solvent treatments of stand oils are claimed to render them more light fast. The effect of resins is variable.

Faucett, P. H.

SOME LETHODS OF ATTAINING SPEED IN VEHICLES CONTAINING OILS. Drugs, Oils & Paints 53, 322, 324, 326, 359-60 (1938); C.A. 33,414 (1939).

"A discussion of O carrier solvents emphasizing the value of pinene for the purpose. By blowing with air the pinene in turpentine can be temperarily charged with enough 0 to multiply its effect several hundred % and its aid to decompn. does not continue after it is dry. The use of adjusted ratio solvents affects the quality of the finished coat. This adjustment of solvent ratios causes a evelonic motion in the film which will tend to carry O to its inner parts, thereby promoting thorough drying, less wrinkling and better pigent distribution in the paints. The (--CH=CH--CH2--CH=CH--) group that occurs 4 times in duodecapentanoic acid or clupanodonic acid with C=O to complete one group may have a configuration which brings the double bonds to practically the same distance apart as in eleostearic acid, making possible a synthesis similar to the diame of the tung oil but with the production of a larger ring. With so many double bonds to the mol. the resistance to approach, as well as the reactivity, would be expected to be very favorable to reactions involving phenolic resins or other oil mols. The greater length of the acids in fish oils may account for their greater flexibility in film. and the large percentage of the acids of low conce. may account in part for the permanence and durability

of films made from them when properly cooked and linked together. Oils contg. 3 conjugated double bonds per fatty acid which offer advantages in attaining speed of drying in oil vehicles are tung oil, Japanese tung oil, Dutch Indian tung oil, Pe-Yoak oil, oiticica and cashew nut shell oil. Ibid. 359-60.--Essang and lumbang oils are also in this class. The conjugated bonds of tung oil can be obtained from castor oil by dehydration of the oil with heat. As the temp. of a batch of oil or of oil and other components is raised the principal phenomena (other than polymerization at the higher temps.) noted are: the increase in speed of rotation of the mols. and the vibration of their parts in different ways as different energy states are reached and as different infrared and heat rediations reach the parts of the mols. which will respond to other particular frequencies." From C.A.

Fearnley, Geo.

A COMPARISON OF OCTOATE AND NAPHTHENATE DRIERS. Official Digest Federation Faint & Varnish Production Clubs No. 290, 137-43 (1949); C.A. 43, 6431 (1949).

"Pb, Mn, and Co drivers were compared in raw linseed oil, phenolic China wood varnish, short oil alkyd vehicle, and Dammar and maleic-dehydrated caster white enamels, for drying time and color change. There were no important differences in most cases. The lower solids content of the octoate (2-ethyl hexanoste) solns. at the same metal contents may be advantageous." From C.A.

Fokin, S.

CATALYTIC OXIDATION AND REDUCTION OF ORGANIC COMPOUNDS. Z. angew. Chem 22, 1451-1459; 1492-1502 (1909); J. Soc. Chem. Ind. 23, 393 (1909).

"The author gives details of the experiments on which were based his conclusions on the drying of fatty oils (this J. 1149 (1907); 98 (1909)). He now groups certain metals found an to accelerate the oxidation in an order different from that proviously given: - (1) Cobalt, manganese, chromium, nickel, platinum, palladium. (2) Barium, load, corium. Where these metals effect a reduction their arrangment is in the reverse order. The phenomonon of a simple absorption of oxygen by unsaturated compounds, without the formation of decomposition products, may be brought about through the agency of metallic oxides. In such cases only about 1/2 of the theoretical amount of oxygen is absorbed, i.e. the autoxidation is semi-molecular. Thus in an experiment with tung oil the absorption of oxygen in a film test, with a cobalt salt as the siccative, reached 8.6 per cent in 24 hours, or "approximately half the theoretical amount (10 per cent)." In a second experiment the plate was heated to 40° C. for 5 minutes, after having been exposed for 3 hours, and the increase in weight after 26-1/2 hours was then 18.7 per cent; so that there was molecular autoxidation." From J. Soc. Chem. Ind. (abridged).

Fokin, S.

CATALYTIC OXIDATION AND REDUCTION OF UNSATURATED ORGANIC COMPOUNDS. J. Russ. Phys. Chem. Soc. <u>40</u>, 276-321 (1911)*; Chem. Zentr. <u>1908</u>, II, 1995-6.

Compounds of metals are considered to cause catalytic oxidation by the conversion of the metals to higher unstable metal oxides which transfer 0 to unsaturated compounds. It is a monomolecular reaction in the case of the oxidation of tung oil, sunflower oil, almond oil and the fatty acids of linseed oil. Catalysts (dryers) used were compounds of Co, Mn, N., Ba, Pb, Ca, and Cr. The Co and Mn were best; Pb and Ca, poorest. There was no linear relation between catalyst concentration and activity.

Friend, J. N. and Davidson, W. J.

OXIDATION OF THE DRYING OILS.

Chem. News 106, 10 (July 5, 1912).

On exposure to the sir in thin films Chinese wood oil increased in weight to a maximum, after which it slowly began to lose in weight.

Frilette, V. J.

DRYING OIL AND OLEORESINOUS VARMISH FILMS. INCREASE IN ACIDITY ON AGING.

Ind. Eng. Chem, <u>38</u>, 493-6 (1946); C.A. <u>40</u>, 4230 (1946).

"Lack of a suitable method for detg. acid nos. of oil and varnish films has retarded the investigation of the fundamental chem. changes that occur during the life of such films. An accurate semimicro titration method was developed, and changes in acidity of the films were studied by this method. Air-dried oil and oleoresinous films rapidly develop acidity, about half of which can be extd. with MeOH. Alkeli resistance is detd. mainly by the acid values of the films. Resins appear to act as diluents, the acidity arising mainly from oxidation of the oil. Phenolic resins inhibit acidity formation more than other resins. Tung oil develops much less acidity than linseed; this accounts for its use in alkaliresistant formulations. Wrinkling and disintegration by NaOH soln, are both evidences of swelling and are equiv. in evaluating alkali resistance. Oleoresinous coatings dried by baking do not develop acidity on drying. This last conclusion substantiates previous statements that chem. reactions involved in baking and air-drying differ." From C. A.

Fritz, Felix

CRACKING OF WOOD CIL FILMS.

Farbe u. Lack <u>1930</u>, 149*; C.A. <u>24</u>, 3386 (1930). "Depending upon circumstances, dried wood oil films may exhibit cracks as described by Eibner and Rossman (C.A. <u>23</u>, 1516) or a folding without cracks." From C. A.

Fritz, Felix

THE BEHAVIOR OF OXIDIZED TUNG OIL. Farbe u. Lack <u>1933</u>, 400; C.A. <u>27</u>, 5557 (1933). "Tung oil, blown at 100° for 6 or more hrs., dries with a clear film and may be used in varnish making." From C.A. Fullor, E. S.

OXIDATION OF SOLID FILMS OF TUNG OIL. Ind. Eng. Chem. 23, 1458-62 (1931); C.A. 26, 865 (1932).

"With polymerized films of tung oil the coloration made by baking requires 0 or oxidized substances in the film. On this basis and on the assumption that the light absorption at any given wave length is proportional to the amt. of 0 reacting, the oxidation of tung oil films at 275-350° was studied by means of their transmission change. The reaction is heterogeneous for film thicknesses of 0.007 to 0.40 mm. The reaction with gaseous 0 is inhibited at the start similarly to that encountered with drying oils at lower temps. The rate of darkening of the film is dependent on the rate of chem. reaction and the rate of 0 diffusion." From C.A.

Gardner, H. A.

VALUE OF CERTAIN PAINT OILS. J. Franklin Inst. 171, 55-72 (1911); J. Soc. Chem. Ind. 30, 223 (1911).

"In the drying tests here described the oils were exposedin the lids of tin canisters about 3 inches in diameter so as to obtain films corresponding more closely than the ordinary films on glass with the layers of paint in practice. The covers containing the test samples were placed on perforated shelves in a box which had glass sides and was provided with an opening through which passed a continual current of air previously dried by means of sulphuric acid. The oxygen absorption was determined by ascertaining the increase in weight at intervals during a period of 20 days, and similar tests were made in a current of moist air. Since tung oil forms a soft opaque film on exidation, special processes are required to render it suitable for ordinary paints or varnishes. The author has found that lead tungate, precipitated from saponified tung oil with lead acotate, yields, when dried and fused with a small proportion of colophony and borate, a drier that gives a perfectly transparent film." From J. Soc. Chem. Ind.

Gardner, H. A.

QUICK POLYMERIZATION AND CXIDATION EFFECTS ON OILS. Ind. Eng. Chem. 22, 378-9 (1930); C.A. 24, 2620 (1930).

"A special app., consisting of a revolving metal drum making a complete revolution in approx. 30 min. and a 51-cm. Hg-quartz tube of the low-pressure type, is employed at the Inst. of Paint and Varnish Research in Mashington, D.C. Much quicker drying offects result when about 0.02% of metallic Co, as a catalyst for the oxidation and polymerization effects, is present. Perilla and linseeds oils contg. 0.02% Co became solid in 24 hrs., and tung oil in 4 hrs. These products extd. with hot acetone yielded 20, 32, and 16%, resp., of unpolymerized products. The polymerized, sponge-like residue was dried and used to det. the amt. of petroleum distillate which could be absorbed. Perilla absorbed 70%, linseed 80% and the tung oil 160% of the mineral spirits before the surfaces of the particles appeared to be wet. These preliminary results indicate the possibility of producing in an economical manner these solid products from oil." From C. A.

Gebauer-Fuelnegg, E., and Konopatsch, G.

COBALT DRIERS.

Ind. Eng. Chem. 23, 163-5 (1931); C.A. 25, 1398 (1931).

"With the hope of getting an insight into the action of siccetives, simple Co compds. of definitely known structure were prepd. and tested as catalysts on China wood oil. Their solns. in org. solvents are efficient drivers in a number of cases. Some such siccetive solns. caused the formation of glass-clear films of China wood oil. A table is given showing the Co compds. and the solvents used. The photomicrographs of the dried films are characteristic of each of the solvents used. Possible explanations are offered of the phenomena encountered." From C. A.

Gee, G. and Rideal, E. K.

CATALYZED POLYMERIZATION IN MONOLAYERS OF DRYING OILS. J. Chem. Soc. <u>1937</u>, 772-8; C.A. <u>31</u>, 8341 (1937).

"The mechanism of the pos. and neg. catalysis of polymerization was studied by the phase-boundary-potential method (C.A. 30, 2025). Films of maleic anhydride- β -eleostearin addn. product (I) on 0.01 N H2SO4, were treated with 0,005% Cott and with 0,1% quinol. The potential at const. surface pressure was const. in the latter case but progressively decreased in the other and for the untreated film. Extrapolation indicated that all 3 systems had the same original potential and therefore that the potential of the unoxidized film wes unaffected by the catalysts. The potential of the oxidized film, contg. either the unstable or the stable peroxide, decreased 15 and 22 mv., resp., when treated with quinol and Co; this indicated complex formation, Conclusion: Polymerization catalysis involves the formation of a complex with the catalyst, while oxidation catalysis does not require this mechanism. Methyl eleostearate autoxidized as a monolayer but ethyl myristate, methyl linoleate and ethyl linolenate did not. All retarded the polymerization of monolayers of I with efficiency decreasing with increasing satn. Data were analyzed by a modification of the method of Jeu and Alyea (C.A. 27, 1800). Conclusion: The polymer chain length rerely exceeds 10 units and is probably less than 5." From C, A.

Greaves, J. H.

FROCESSING OF DRYING OILS, RECENT DEVELOPMENTS. Official Digest Federation Paint & Varnish Production Clubs No. 237, 359-67 (1944); Oil & Colour Trades J. 105, 579-82 (1944); Paint Ind. Mag. 59, 208-11 (1944)*; C.A. 38, 4142 (1944) (no abstract).

The excellent drying properties of tung oil are explained as being due to the presence of conjugated double bonds. The processes which create conjugation of double bonds in castor oil by dehydration and in other oils by alkali isomerization, and the various efforts to concentrate the most unsaturated components of other oils are reviewed.

Gregg, G.W. and Anderson, L.E.

EFFECT OF DRIERS ON THE CHEMICAL AND WATER RESISTANCE OF AGED VARNISH FILMS. Official Digest Federation Paint & Varnish Production Clubs No. 270,

421-9 (1947); Paint Ind. Mag. <u>62</u>, 262, 264-8 (1947); C.A. <u>41</u>, 6736 (1947).

"Six different drier compns. were incorporated into three commonly used types of varnish, and films from these compns. were tested for resistance to hot and cold H20, 3% alkali solns, and soap soln, after eging for 3, 14, 30, 60, and 90 days. The varnishes used were: meleic/dehydrated castor oil, modified phenolic resins/linseed oil and a 52V17-type varnish contg. phenolic resins and e mixt. of China wood oil and linseed oil. The drier compns. were: 0.05% Co; 0.05% Co and 0.5% Pb; 0.02% Co, 0.5% Fb, and 0.05% Mn; 0.05% Co, 0.5% Pb, and 0.1% Ca; 0.1% Co and 0.01% Pb; and 0.05% Co, 0.5% Pb, and 0.1% Zn. The results showed that a drying vernish film is not likely to reach equil. before 14 days; by the proper selection of driers any short time drying specification test can be met; and drier selection does have an important bearing on ultimate film characteristics. Generally, for any of the above tests on varnish films, critical changes occurred between 3 and 14 days' sging time. Aging tests involving less than three days showed relatively great differences with different drier compns., while tests of more than 14 days' aging showed much less pronounced differences for different driers. The HoO resistance of vernish films improved with age, while the alkali and scap resistance decreased. Drier compns. effective in physically drying the film are likewise resistant to alkali and water." From C. A.

Harrison, A. W. C.

SOME TECHNICAL METHODS OF PREPARING WOOD OIL IN PAINTS AND VARNISHES. Paint Vernish Production Mgr. 34, 9-12, 40 (Sept. 1930).

The drying characteristics of raw and of heat treated tung oils are reviewed with special attention to the effect of gelation inhibitors, acid number and driers.

Harrison, A.W.C., and Fonrobert, E.

BLOOMING OF VARNISH FILMS.

Farben-Ztg. <u>36</u>, 1467-9, 1512-4, 1554-6, 1601-3 (1931); C.A. <u>25</u>, 5046 (1931).

Numerous causes of dull surfaces and cloudiness in varnish films are reviewed. Varnishes containing tung-oil stand oil may exhibit surface drying when thick films containing large concentrations of cobalt or manganese driers are exposed to air currents. Hartman, F. E.

RAPID OXIDATION OF PAINT AND VARNISH FILMS.

Paint Oil Chem. Rev. 76 (23), 10-1 (1923); C.A. 18, 757 (1924). "A H20-proof varnish which dries in 12 hrs. in air at 80°, dried in 6 hrs. at room temp. in air contg. 0.01% 03. Various varnishes dried much more rapidly and hardened more quickly in air contg. 03. Drying time.was detd.by inserting the panels with varnished surfaces facing each other, in a uniform-pressure hydraulic press at const. temp. and noting the time at which the panels no longer stuck together. Films dried in ozone had phys. properties equal to or better than those dried in air. Satd. solns, of varnish gums in xylene were unaffected by bubbling air contg. 0.5% 02 through them for 10 hrs. Linseed, soy, and castor oils were bleached and deodorized by the same treatment: China wood oil solidified after several hrs.: a suspension of FbO was darkened somewhat: suspensions of other pigments were unaffected. A relative humidity of 10% at 70° for air, and of 20% for ozonized air, gave the best hardening conditions for varnish films. In general, drying time of varnishes is decreased 50 to 200% by ozonized air, and it is practicable to employ it for increasing output of commercial varnishing operations. (Details are lacking.)" From C. A.

Hausman, Margaret J.

OITICICA OIL.

Am. Ink Maker 15 (1), 16-19 (1937); C.A. <u>31</u>, 2840 (1937). "Mfg., processing and compounding are briefly described and chem. consts. listed. Comparable to tung oil in performance it provides a more durable and glossier surface, is less resistant to boiling H₂O and less distensible, and remains freer from skinning but is more apt to wrinkle. In crude form it is a viscous solid contg. chiefly glycerides of a triply unsatd. ketonic acid, licanic acid." From C.A.

Hintze, Otto E.

THE PERMEABILITY OF LACQUER FILMS.

Farben, Lacke, Anstrichstoffe 3, 265-70, 291-300 (1949); C.A. <u>44</u>, 851 (1950).

"The relative moisture permeability (R.M.P.) (i.e. water vapor losses through films/free evapn. of water under test conditions) was detd. of clear and of pigmented films of Plexigum B50 lacquer, linseed-oil varnish, linseed-oil stand oil (0.1% Co.), China-woodoil stand oil, nitrocellulose lacquer (contg. Resin AW2, Palatinol C, and tritolyl phosphate), chlorinated rubber (Pergut N) plasticized with Clophen A60, and of a bitumen. R.M.P. was only slightly affected by temp. changes.** The R.M.P. was lowest with bitumen, chlororubber, and nitrocellulose, highest with linseed-oil varnish, and intermediate with the stand oils." From C.A. (abridged).

Hilpert, R. S. and Niehaus, Cl.

PHENOLS AS ANTIOXYGENS IN DRYING OILS.

Z. angew. Chem. <u>47</u>, 86-90 (1934); C.A. <u>28</u>, 2549 (1934). "Expts. were made on the action of some phenols upon the drying of linseed oil and wood oil, with and without addns. of Co, Pb and Mn driers. Uniform conclusions could not be obtained. Exptl. results and twelve references are given." From C.A. DRYING OF CHINESE LACQUER-OIL VARNISHES. Paint Oil Chem. Rev. 81 (15),10-1; (16) 10-1; (17) 10-2; (18);

10-2; (19);10-2; (20) 10 (1926); C.A. 20, 2254-5 (1926).

"The drying of the sap of the lac tree (Rhus vernificifera) alone and mixed with Chinese wood oil and driers was studied. The drying process differs from that of the usual drying oils and also varies with drying conditions. In the presence of moisture, drying is accomplished by initial volatilization, formation of intermediate transition compds. and final oxidation. These steps are accelerated by the action of moisture and the oxidase enzyme "laccase" which is present in the lacquer. In the absence of moisture, the varnishes dry by straight oxidation following volatilization. Temp. as well as humidity plays an important part in the drying, 25° being more favorable than 0° or 40° for the drying of most lacquer-oil varnishes. . Pb, Mn and Co accelerate the drying to about the same extent, the Mn being slightly the best. The optimum amt. of the Mn is about 0.2%. The most favorable condition for drying lacquers is at 25° with 80% relative humidity. The most satisfactory varnish is one contg. 80% Chinese lacquer and 20% bodied China wood oil." From C. A.

Ho, K.

PRELIMINARY STUDIES ON DRYING OF TUNG OILS WITH DIFFERENT DRIERS. Chem. Ind. (China) 7, 1-9 (1932); C.A. 27, 3092 (1933). "Tests using metallic Co, Cu, Mn, Pb, Al and Ni showed that 0.025% Co and also mixts. of Co with Al or Mn are most effective as driers and in yielding a product of the desired transparency." From C. A.

Hyman, J., and Greenfield, T.

CAUSE OF CRYSTALLIZATION OF TUNG OIL VEHICLES.

Ind. Eng. Chem. 28,238-41 (1936); C.A. 30, 2410 (1936).

"Earlier theories of the 'crystallization' of tung oil varnishes are discussed. 'Crystallization' is shown to be caused by as little as 4 parts per million of NO_2 , which is formed from air by the action of flames, sparks or ultraviolet light. O_3 is without action. The yellowing of paints and paper, the fading of inks, and the knocking of motor fuels may also be influenced by traces of NO_2 . App. is described for studying the 'crystallization', which is a very sensitive test for NO_2 ." From C. A.

Kappelmeier, C.P.A.

THE FORMATION OF FILMS OF DRYING OILS.

Chem. Weekblad 28, 174-83 (1931) (in Dutch).

A detailed review of the chemical aspect of the drying of fatty oils.

Kiselev, V. S.

THE EFFECT OF HOT DRYING ON THE PHYSICAL AND CHEMICAL PROPERTIES OF OIL FILMS. II.

Org. Chem. Ind. (U.S.S.R.) 4, 502-8 (1937)*; C.A. 32, 5234 (1938). "Crude, polymerized and oxidized linseed, wood and sardine (ivasa)

oils and dehydrated castor oil and their mixts., with and without the

addns. of solvents and Pb and Mn linoleates, were costed on a surface and then dried at the ordinary conditions and at 120° and 200° for 0.5, 1 and 2 hrs. The comparative tests indicate that oil films obtained by drying at normal conditions and at elevated temps. differ sharply in their phys. and chem. properties. The films formed by hot drying are characterized by a considerable loss in wt. (oxidation) (instead of the usual wt. increment), a sharp lowering of the film reversibility (decreased soly. in acetone), a drop in the acid and I values and an increase in the sapon. value, a greater hardness and resistance to water and retardation of the film aging." From C. A. (abridged).

Kronsbein, W.

THE PRESENT STATUS OF OIL RESEARCH, ESPECIALLY OF THE DRYING PROCESS. Farben - Chem. 2, 373-7 (1932); C.A. 27, 198 (1933).

"A review, especially of the theories of Eibner and Scheiber." From C. A.

The theories considered are applied to the drying of tung, linsced and other oils.

Krumbhear, Wilhelm.

THE BLOOMING OF VARNISH FILMS.

Am. Paint Varnish Mfrs'. Assoc. Circ. <u>370</u>, 520-32; Am. Paint J. <u>14</u>, (52A), 30; Paint Oil Chem. Rev. <u>90</u> (17), 59-62; Oil, Paint Drug Reptr.<u>118</u> (19), 59-60 (1930); C.A. <u>25</u>, 221 (1931).

"Blooming is defined as an iridescence which sometimes appears on fresh varnish films. It is probably due to cryst. oxidation products of the drying varnish and occurs most frequently in rapidly changing atms., such as drafty corriders, etc. Pb, Co and Zn have a tendency. to produce blooming but Ca and Mn do not. To be non-theoming a linseed oil-rosin varnish must contain at least 3 parts of oil to 2 parts of rosin. On the other hand, tung oil behaves as a resin and no amt. will prevent bloom. Sierre Learne, Congo, Brazil, Manila and Kauri gums permit bloom, the amts, increasing with the type of resin in the order named. 'Running' does not decrease the tendency. Synthetic resins and ester gum also permit blooming. High cooking temps., e.g., over 400°F., do not prevent blooming. The nature and manner of using thinners have no effect except that blooming may occur if used at temps. over 400°F." From C. A.

Krumbhaar, Wilhelm.

BLOOMING OF OIL VARNISHES.

Farben-Ztg. 36, 1726-7 (1931); C.A. 25, 5046 (1931).
 "In reply to Harrison and Fonrobert (Farben-Ztg. 36, 1467-9,
1512-4, 1554-6, 1601-3, 1645-6 (1931)). K. states that his work
was exptl. and that no theories were involved." From C. A.

Levy, P.

USE OF BANCOULIER OIL IN PAINTS AND VARNISHES. Recherches et inventions 16,311-12 (1935); C.A. 29,5290 (1935). The drying properties of the oil obtained from the seeds of <u>Aleurites moluccana</u> are compared with those of the oils of <u>A. fordii</u>, <u>A.-montene</u> and <u>A.-cordate</u>. When 100 parts of "Huile de bancoulier" (<u>A.-moluccana</u>) is heated quickly to 280° with 10 to 400 parts of abrasin oil (<u>A.-montana</u>) coatings are obtained which dry in 4-14 hours, those highest in abrasin oil drying fastest.

Light, L., and Barry, T. H.

ANTI-SKINNING AGENTS.

Official Printing Ink Maker 4 (3), 10-1, 22, 24 (1934); C.A. 28, 3916-7 (1934).

"An effective anti-skinning agent must fulfil the requirement of reducing oxidation in the container to a min. without at the same time seriously slowing down the rate of drying of the material in the film form. Up to now this agent has been used in either of 2 forms (a) actual solvents such as dipentene and methylcyclohexanol or (b) catalytic antioxygen agents such as pyrocatechol and guaiacol." From C. A.

 β -naphthol reduces skinning of tung oil preparations only when the latter are made with neutral resins. It does reduce the tendency to "gas-check".

Ludwig, G. E.

THE CATALYTIC EFFECT OF LEAD AND MANGANESE ON THE DRYING OF CHINA WOOD OIL.

Ind. Eng. Chem. 17, 1160-1 (1925); C.A. 20, 994 (1926).

"In a '25 gal.' rosin-wood varnish, 0.26% Pb, or 0.03% Mn is the most efficient amt. of these metals when used alone to secure the max. drying rate. The metals in the form of PbO and of Mn borate, resp., were incorporated hot into the varnish base. Drying time curves for varying concns. of metal are given." From C. A.

Merz, Otto

WOOD OIL, TUNG OIL, CHINA OIL, ETC.

Kunststoffe 15, 215-6 (1925); C.A. 21, 1716 (1927).

"A microscopic examination of the so-called ice flower formation by the drying of Chinese wood oil showed that this also was due to the formation of wrinkles." From C.A. (sbridged)

Mechanisms of drying of tung oil and methods of determining its purity are carefully reviewed.

Merz, Otto

THE OPAQUE DRYING OF CHINESE WOOD OIL.

Farbe u. Lack <u>31</u>, 332-3, 343-4 (1926); C.A. <u>21</u>, 184 (1927).
"The recent literature on the drying of wood cil is reviewed.
M.'s exptl. work covered the drying of raw wood cil, bodied cil, with end without driers, and crystg. wood cil varnish under various combinations of daylight, ultra-violet light and other atm. conditions. His results indicate that ultra-violet light as such does not cause the opaqueness in the film. Drying is accelerated by light, retarded in darkness. Slow drying (as in a closed desiccator) produces clear, non-wrinkled films." From C. A.

Milligan, J.

CHEMICAL EFFECT OF WATER ON DRYING-OIL FILMS. J. Oil & Colour Chemists' Assoc. <u>19, 59-61</u> (1936); Brit. Chem. Abstracts <u>1936</u>, B, 379.

"All linseed and tung oil films made by the author were found to undergo destructive liquefaction (hydrolysis) under prolonged conditions of heat (78-80°) and (100%) R.H., the early stages of the process being related to the toughening accompanying ageing. Highly polymerised (e.g., stoved) films are more stable than oxidised (air-dried) films." From the Brit. Chem. Abstracts

Morrell, R. S.

YELLOWING OF DRYING OIL FILMS.

J. Oil & Colour Chemists' Assoc. <u>10</u>, 186-201 (1927); C.A. <u>21</u>, 3274 (1927).

"Recent literature on the yellowing of paint oils is reviewed. A no, of paint films were prepd. using Zn white, Ti white. timonox, lithopone, white lead, As_2O_3 , SnO_2 and, as oils, poppy seed, walnut, stand oil, β -eleostearic glyceride, China wood, raw linseed, bleached raw linseeds. Tintometer readings are given for several months yellowing, and comparisons are made. The work of pravious investigators is generally confirmed. Of the white pigments exand., white lead shows a greater tendency to produce yellowing than ZnO, and anhyd. TiO₂ is the best. The use of the cryst. glyceride of China wood cil gave promising results as a paint medium and its chemistry is reviewed. From data obtained in the oxidation of this glyceride the yellowing in the dark is probably connected with the presence of hydroxyl groupings (derived from the peroxide) contiguous to the carboxyl end of the mol. The use of inactive anhyd. pigments is recommended to reduce yellowing." From C. A.

Morrell, R. S.

ACTION OF ALPHA-NAPHTHOL AS A NEGATIVE CATALYST IN OXIDATION OF DRYING OILS.

Paint Varnish Production Mgr. 34, 12, 14, 17, 31 (Dec. 1930). a-Naphthol inhibited the formation of bloom on linseed oil cr tung oil varnishes and also retarded their drying as indicated by reduced rates of increasing in weight and of herdening.

Morrell, R. S., and Marks, S.

THE DRYING OF OILS,

J. Oil & Colour Chemists' Assoc. <u>12</u>, 183-205 (1929); C.A. <u>23</u>, 4824 (1929).

"Recent theories of the drying of oils are discussed and the conclusion is reached that oxidation is followed by polymerization and gelation. Pure β -eleostearin was oxidized in the solid state and in soln. in C6H6 and in COl4. The results of oxidation in the solid state were not satisfactory. Oxidation in soln, resulted in an insol gel (I) and sol, portion (II). I is a monoperoxydi-hydroxy- β -eleostearic glyceride, while II contains a petrolaum ether insol, form (F) and a sol, form (E), in which the hydroxyl groups of I have passed into the keto form and in which the peroxy

group has disappeared. I yields a polymerized methyl ester (A), insol. in petroleum ether, and a simple methoxy methyl ester (C), sol. in petroleum ether. II yields corresponding products (G) and (H). The mol. wt. of A is 1107 (calcd, 1068) indicating that the oxidized gel was intramolecularly polymerized. The formation of C destroyed the polymerization, indicating that polymerization is assocd. with the hydroxyl groups. In all of the compds mentioned, the I value indicates one remaining double bond. Sapon. nos. of I, A and C were high (over 300) indicating disruption of the mol during sapon. I is insol. in C6H6, CCl/, EtOAc and Me2CO. It is slowly scl. in valeraldehyde which fact may account for the gradual softening in some cases of drying-oil films. When fresh it is sol. in glacial AcOH. On heating, it decomposes with formation of valeraldehyde. Piperidine unites with the gel to form a soln. which may be diluted with H20, C6H6 or alc. The union with piperidine decomposes with evolution of piperidine and formation cf valeraldehyde." From C. A.

Munzert, H.

YELLOWING OF WHITE ENAMELS.

Farben-Ztg. 33, 2849-51 (1928); C.A. 23, 1761 (1929).

"Previous German work on the yellowing of enamel vehicles with age is summarized. A series of comparable enamels was prepd., using equal bulks of ZnS ('sachtolith'), titania, ZnO and white lead, all in a high state of purity, with each of the following vehicles (white spirit being the solvent): 60% soln. of limehardened rosin, 60% soln. of ester gum, 70% soln. of pale linseed cil stand oil, and 60% soln. of a tung oil-linseed oil stand oil. The 16 enamels were brushed on tin plate, and dried for 4 days in diffused daylight. The films were then half-covered by black paper and exposed to direct sunlight for 14 days, after which the degree of yellowing was noted in comparison with freshly prepd. films of the stored enamels and with films of similar freshly prepd. enamels. The covered films were found to yellow more than the exposed ones, while of the pigments white lead caused most yellowing, followed by ZnO, titania and ZnS in descending order. Yellowing is attributed in the main to dark-colored oxidized acids which rapidly undergo further degradation in the light to form geseous or colorless compds. This degradation is, however, delayed in the dark and to a greater degree still by salt formation with pigments, the 'fixing' of the yellowing being proportional to the basic nature of the pigment." From C. A.

Nelson, H. A.

REPORT OF COMMITTEE D-1 ON PRESERVATIVE COATINGS FOR STRUCTURAL MATERIALS. REPORT OF SUB-COM. IX ON VARNISH. Am. Soc. Testing Materials Froc. 23, I, 290-9 (1923); C.A. <u>18</u>, 1207 (1924).

Physical properties of varnish films are indicated by stress-strein measurements. Distensibility, tensile strength and nature of the break are reported for the following 4 types of varnishes: (a) China wood oil - ester gum, (b) Linseed oil - Kauri gum, (c) Linseed oil limed rosin, (d) China wood oil - limed rosin. Nolte, H.

NON-BLOOMING VARNISHES

Farbe u. Lack <u>1932</u>, 413-14, 425-6, 439-40; C.A. <u>26</u>, 5775 (1932). "Bloom on a varnish film takes the form of a fine pale blue or white deposit and must not be confused with loss of gloss through mech. defects or chem. destruction of the film. It is due, especially to changing atm. conditions during drying. Dampness is a predominating cause. Thick films often are responsible. Bloom-free varnishes cannot regularly be prepd. with ester gum and linseed oil; but limed rosin may be used if not in too great an amt. Other suitable resins are Albertols, Sierre Leone and Pontianak copals. Tung oil has a bloom-producing tendency. Co, Mn and Pb driers may all be used in moderate amts." From C. A.

Nonaka, Masao

DRYING OF TUNG OIL.

J. Chem. Ind. (Japan) 24, 1272-96 (1921)* (in Japanese); C.A. <u>16</u>, 2418 (1922).

"The tung oil used was from <u>Aleurites fordii</u>. The oil was about 1 year old, and had d15.50.944, sapon. no. 188, I no. 164.2, acid no. 2184, Reichert-Meissí value 1.4 and contained 0.75% unsapon. substance. The mixed fatty acids were composed of 82.5% eleomargaric acid, 15.0% cleic acid and 2.5% stearic acid. Conditions that influence the drying of this cil were investigated. The speed of drying is inversely proportional to thickness of the oil. In daylight it dried in 5 days; and contrary to general belief, it dries even in dark (50 days). In absence of air or in a CO2 atm. it dries, High humidity retards drying, and its wt. increases. The higher the temp. the more quickly it dries. Driers accelerate the drying in proportion to their quantity. Manganese drier is more effective in dry air than lead drier, but in moist air lead drier is more effective. When the oil is heated, it becomes a viscid transparent, yellow solid. In absence of air it solidifies in 6.3 hrs. at 200°, instantaneously at 250°, but in the air, it requires 11 hrs. at 150° and 3.5 hrs. at 200°. It does not increase in wt. until it dries, then its increase is rapid. CO2 and unsatd. compds. are found in the decompd. product of the drying. One of the double bonds of eleomargaric acid is easily oxidized. Drying of the oil is due not to oxidation, but to polymerization and condensation. In consequence of polymerization and condensation of unsatd. acids, mols. are aggregated and colloidal soln. is produced. Oxidation accelerates drying indirectly by forming condensation products of the exidized product. The results of microscopic examn. of dried . films are reported." From C. A.

Overholt. J. L., and Elm. A. C.

FORMATION AND DETERIORATION OF PAINT FILMS. CHANGES IN THE GLYCERYL ESTERS OF SEVERAL UNSATURATED FAT ACIDS UNDER EXPOSURE TO ULTRA-VIOLET LIGHT.

Ind. Eng. Chem. <u>33</u>, 658-60 (1941); C.A. <u>35</u>, 4225 (1941). "The glyceryl esters of oleic, linoleic, linolenic, and eleosteeric

acids used in these tests were prepd. from the Me esters. The changes

in the films of these esters were detd. by the methods previously described (C.A. <u>34</u>, 8300). The rate of gain in wt. of the glyceryl esters is almost identical with the Me and glycol esters. However, on prolonged exposure the glycerides lost less wt. than the glycol esters. The I values indicate that these esters are oxidized in 4, rather than 3, steges namely, induction period, rapid oxidation ending in drying, a slow continued 0 obsorption and finally a period of little change. The glycerol oleate remained a viscous liquid, the others formed dry, difficulty sol. films. The mol. wt. of the glycerol oleate decreased sharply after 110 hrs. of exposure, which indicates appreciable decompn. If a dry film forms the ester is moderately resistant to further decompn., if not it oxidizes further and decomps. to acid and hydroxy compds." From C. A.

Pittsburgh Paint & Varnish Production Club.

A STUDY OF SCYA-TUNG OIL COMBINATIONS.

Paint Oil. Chem. Rev. <u>110</u>, (23), 99-103 (1947); Official Digest Federation Faint Varnish Production Clubs No. <u>275</u>, 725-34 (1947); Paint Ind. Mag. <u>63</u>, 16-22 (1948); C.A. <u>42</u>, 3587 (1948).

"Blends of soybean and tung oils (80:20, 60:40, and 40:60) were bodied at 550°F., 575°F., and 600°F. The 40-60 blend jelled at 575°F. and 600°F.; the 80-20 blend exhibited poorer drying than bodied linseed oil; the 60-40 blend produced equal or better drying properties than bodied linseed. Better film hardness on aging is exhibited by blends bodied together than by blends of oils each bodied separately before blending." From C. A.

Pittsburgh Paint and Varnish Production Club.

A STUDY OF SOYBEAN OIL-TUNG OIL COMBINATIONS.

Official Digest Federation Paint Varnish Production Club No. <u>286</u>, 854-8 (1948)*; Paint Oil Chem. Rev. <u>111</u> (23), 73-4, 76-7 (1948); C.A. <u>43</u>, 3212 (1949).

"Copolymerized soybean oil and tung oil (in the ratio 67:33) dried at approx. the same rate as linseed oil of the same, dried slightly more slowly in varnishes to give a film of slightly lower Sward Hardness rocker reading and of equal water resistance. Prebodying of the soybean oil before co-bodying with tung oil improves the drying time, but ester interchange between oils by heating at 425°F. before increasing heat for bodying does not increase drying speed. All results are tabulated." From C. A.

Quincke, F., and Kamphausen, K.

MOLECULAR AND ABSOLUTE DRYING ACTION OF VARIOUS METALS. Farbe u. Lack 1927. 341-3; C.A. 22, 3054 (1928).

"The usual method of detg. the relative dryness of paint films with the fingers does not give const. results. Q. and K. successfully used for this purpose the capillary action of filter paper. The height of rising of the oil gives a direct measurement for the drying action of the metal whose salt was used as drier. The amt. of drier necessary to obtain the optimum drying action is proportional to the mol. weight of the corresponding metal and is 0.003 mol. per 100 g. linseed oil. Charts and tables are given showing the drying action of various metals in combination with linseed (a) the tung cil (b) in the presence of a drier is given in fraction of the drying time of the drier-free oil. 1/30 to 1/15: a) Co: b) Co, Fe, Mn, Cu. 1/10 to 1/4; a) Mn, Pb; b) Cr, Pb, Zn, Ni 1/2: a) Fe, Ni, U, Cr; b. 3/4: a) Bs, Cu, Mg, Sr, Mox, Zn, Ca, W; b) Bs, Mg, Sr, Cd." From C. A.

Redman, L. V., Weith, A. J. and Brock, F. P. DRYING RATES OF RAW PAINT OILS. J. Ind.Eng. Chem. 5, 630-636 (1913); J. Soc. Chem. Ind. 32, 874,

(1913).

"Experiments were made with two samples each of linseed, soys bean, and China wood (tung) oils and four samples of fish (menhaden) oil. Films were painted on glass and these were exposed to a current of filtered air for 20 days in diffused daylight. The results are given in curve-diagrams showing (1) the gain in weight of the oils, and (2) the daily variation in weight together with the variation in temperature and relative humidity of the air. The linseed, soya been and tung oils gave solid films in 20 days, but the fish oils remained tacky viscous liquids. The fish oils gained in weight much more rapidly, and the maximum gain in weight (average, 12.5 per cent on the third or fourth day) was greater than with the other oils, viz., linseed (11.5 per cent on the seventh day), soya bean oil (7.7 per cent on the sixth day), and tung oil (10.5 per cent on the ninth day). The increase in weight was most rapid on the fourth and seventh days for the linseed oils, in the first two or three days for the fish oils, on the fifth day for the soya bean oil, and on the fourth and fifth days for the tung oils." From J. Soc. Chem. Ind.

Reutenauer, G.

CURCAS OIL AS SUBSTITUTE FOR DRYING OILS.

Bull. mens. ITERG (Inst. tech. études et recherches corps gras) <u>1948</u> (5) , 32-3*; C.A. <u>42</u>, 6546 (1948).

"Systematic investigation of the drying properties of curcas oil (I), iodine no, 93, sapon. no. 190, in mixts. with: linseed oil (II), II standolized by heating for 4 hrs. at 300° (III), China wood oil (IV), and IV standolized by heating a few min. at 270° in a current of CO_2 (V). To each 100-ml. sample 0.08 g. Pb as Pb naphthenate were added, and the drying power was examd. by exposing it on an inclined glass plate until impression of the finger left no trace. The tabulated results show that the drying time of I of 4 days is increased to 8 and 6 days, resp., if 20% of I is added to II and III and to 12 and 10 days, resp., for IV and V are exactly doubled by 20% of I and approx. quadrupled by 40%; 60% of I in V (drying time 4 days) is a limit; further increase brings about an incongrous augmentation of the drying time (12 days for 70%)." From C. A.

Rhodes, F. H. and Ling, T. T.

THE OXIDATION OF CHINESE WOOD OIL. Ind. Eng. Chem. <u>17</u>, 508-12 (1925); C.A. <u>19</u>, 1783 (1925). "The total O absorption and the evolution of volatile matter of raw and treated tung oils were detd. by the method of Rhodes and Van Wirt, and are graphically presented. The drying of tung oil is due to an autocatalytic oxidation with formation of a solid oxidation product. Raw tung oil absorbs 44% 0 in 500 hrs., and evolves 36% volatile matter; bodied tung oil absorbs 29.5% 0 and evolves 18% volatile matter, so that the net gain in wt. is approx. the same as that for raw oil. Co appears to be the most effective drying catalyst since it accelerates the initial oxidation of the oil, and increases the total amt. of O absorbed. Pb drier shows a short induction period of drying, and Mn drier, a very pronounced induction period. Tung oil bodied with rosin and with paracoumarone resin oxidizes in two distinct stages: after about 2.5% O has been taken up in 45 hrs., the absorption ceases for about 20 hrs., and then again resumes rapidly. The drying point of the mixt. coincides approx. with this break in the oxidation curve. The addn. of Co drier to resin-tung oil mixts. eliminates this break in the O-absorption curves." From C. A.

Rinse, J. and Wiebols, W.H.G.

SWELLING OF DRYING-OIL FILMS IN WATER.

Ind. Eng. Chem. 29, 1149-54 (1937); C.A. 31, 8955-7 (1937). "The oil to be examd. was painted 30µ thick on tin plates, dried 14 days and immersed (in duplicate) in descrated running tap water at 30°. The soaked films were dried with filter paper and rapidly weighed. The accuracy was 1-2%. For linseed oil (I) there was sometimes a net loss of weight (greater with Go than Pb drier) owing to exidation and leaching. The superiority of tung oil (II) was quantitatively confirmed; e.g. bodied II a max. of 5%, bodied I 180 to 349%. Oiticica oil (III) was next to II in water resistance, then synourin (IV) (dehydrated castor oil). Films of I, bodied or not, absorbed most water with a Fb drier, less with Mn and least with Co. This order was reversed with II, III and IV. This is explained by stating that Pb is the best catelyst for polymerization (drying of II), Co best for exidation (drying of I)." From C. A.

Rossmann, E.

THE TUNG OIL PHENOMENON AND THE DRYING OF OILS WITH IONIZED OXYGEN. Farben-Ztg. 38, 1288 (1933); C.A. 27, 5557 (1933).

"When ionized O was present during the drying of tung oil, wrinkles were formed in the film, but ionized N or illuminating gas produced no wrinkling. Ionization may be effected by a flame, ultra-violet light or radioactive materials." From C. A.

Rossmann, E.

CORNIFORM CRYSTALS.

J. Soc. Chem. Ind. 53, 135-7T (1934); C.A. 28, 4644 (1934).

"When tung oil is allowed to dry while strongly illuminated corniform crystals occasionally form at the surface of the oil, and become amorphous in time. They are regularly constructed, uniformly inclined to the right, and form star-shaped clusters. The surface crystals are believed to possess no higher degree of symmetry than the individual mols." From C. A. Scheiber, Johannes.

THE INFLUENCE OF HEAT AND THE DRYING PROCESS OF FATTY OILS. Ferbe u. Lack <u>31</u>, 295-6 (1926); C.A. <u>21</u>, 184 (1927).

"A preliminary communication on the chemistry of the drying process of linseed and China wood oil. The relation between heat bodying and 0 formation in drying is emphasized. The exptl. part and bibliography will be given later." From C. A.

Scheiber, Johannes

INFLUENCE OF NEGATIVE CATALYSIS ON THE STRUCTURE OF PROTECTIVE PAINTS.

Ferben-Ztg. 33. 680-2 (1927); C.A. 22, 2670 (1928).

"The preventive action of products such as phenols, amines, derivs. of hydroxylamine, hydrazine and urea toward oxidative decompn. of a linseed oil film in the presence of a drier may be fully utilized by applying paints which contain besides linseed oil and driers an anticxidant and oils, such as tung oil. In such a compn. the linseed oil is the continuous phase and is protected from oxidation by an excess of an antioxidant. The tung oil, capable of coagulation without the aid of O_2 , but under the influence of a catalyst, such as is formed by a drier, represents the disperse phase." From C.A.

Scheiber, Johannes.

VEHICLES FOR PAINT AND VARNISH. Forbe u. Lack <u>1928</u>, 68-9, 80-1, 93-4, 106 (1928); C.A. <u>22</u>, 2670 (1928).

"S. classifies vehicles as follows: aq. reversible-glue; aq. irreversible-water glass; non-aq. reversible-spirit varnishes; nonag. irreversible-oleoresinous varnishes; and finally emulsions. He also classifies them as gel, associated colloid, resins, raw oils and processed oils. Wood oil dries by polymerization at its conjugated double bonds and the product is stable toward oxidizing compds. Linseed oil dries by oxidation and breaks down more rapidly than wood oil. Negative catalysts should be added in one of two different ways; to dried film, which is difficult or in a passive condition to the original oil, becoming active after the film is dry. Dried st 100° wood oil sets in 8-12 min. while perilla, linseed and poppyseed oils require 1-6 hrs. When dry the changes in wt. are, resp., 0, 3-7, 14 and 30%. Linseed oil films are affected by water on account of the water-sol. products of oxidation. To overcome this, bases forming water-insol, products may be added. Rust-preventive paints usually contain pigments which combine with the decompn. products of the oil. Acid-resisting coatings are easier to prep. than alkali-resisting ones as most materials are sapond. by alkali." From C. A.

Scheiber, Johannes.

WOOD OIL AND WOOD OIL SUBSTITUTE.

Farbe u. Lack 1929, 153-4; C.A. 23, 3358 (1929).

"The instability of pure wood oil films is due to the eleostearic acid and its triply conjugated bonds, which imparts pronounced polymerization characteristics. These polymerization characteristics eventually lead to the destruction of the film. If the elements of water be removed from ricincleic acid by appropriate means an acid with doubly conjugated bonds results. This acid may be readily esterified with glycerol to form a drying oil with many of the desirable and with but few of the undesirable properties of wood oil." From C. A.

Scheiber, Johannes.

DRYING OF FATTY OILS.

Ferbe u. Lack 1929, 477-8; C.A. 24, 251 (1929).

"S. disagrees with Scheifele that the drying of oils is independent of oxidation. Tung oil, e.g., may set without, but final hardening depends upon oxidation. After 190 days, the yield of CO_2 from a drying tung oil film is of the same order as that from other oils." From C. A.

Scheiber, Johannes.

THE DEVING AND YELLOWING OF LINOLENIC TRIGLYCERIDE. II.

Farbe u. Lack 1931, 511-2; C.A. 26, 3684 (1932).

"Films of linseed and tung oils, and of the synthetic triglyceride of octadecadiene 9, 11 acid 1 (Scheiber oil, C.A. 23, 3358, 5051) contg. (a) Co and (b) Pb-Mn driers did not yellow within 2 years when stored in a desiccator, but did so within a few months when stored in the ordinary lab. atm. The yellowing is ascribed to oxidation promoted by H₂O as a carrier. Subsequent bleaching in strong light is a reduction process. Impurities are without effect." From C. A.

Scheiber, Johannes

THE IDEAL CONSTITUTION OF A FATTY DRYING OIL.

Farbe u. Lock 1935, 411-13, 422-3*; C.A. 29, 8365 (1935).

"A discussion of the drying properties of various fatty oils leads to the following conclusions: Unsatd. fatty oils whose double bonds are not conjugated produce excessive amts, of decompn. products during drying. Fatty oils contg. acetylenic linkages, e.g., the triglyceride of 9-octadecine-carboxylic acid, are devoid of drying power. Tung oil, on the other hand, has such a strong tendency toward oxidation and polymerization that it is often impossible to avoid undesirable effects during film formation. The synthetic triglyceride (I) of 9,11-octadecadienecarboxylic acid (II) is characterized by an unusual combination of desirable properties. I dries with a min. of decompn. to form a film having unexcelled phys. properties and stability. The oxidation of I is subject to easy control by driers or antioxidants. Mixed glycerides contg., e.g., 2 residues of II and one of 9,11,13-octadecatrienecarboxylic acid, from tung oil, also have unusually advantageous drying characteristics." From C. A.

Scheiber, Johannes.

THERMALLY FORMED OIL FILMS.
Farbe u. Lack <u>55</u>, 35-40 (1949); C.A. <u>43</u>, 5203 (1949).
 "Chinawood oil (I) is inferior to linseed oil (II) for use in
baking varnishes. The drying mechanism of I, probably a diene

condensation catalyzed by peroxides formed in the oil, does not very with the temp. I films dry in 51 hrs. at 20°, in 10-12 min. at 100°, and in 1-2 min. at 180°, confirming calons. Further heating of dry I films at 160° makes them turn brittle and lose adhesion. On air exposure at 20°, I films lose only 1.5-3.3% (as CC2) in a year; at 100°, 11.3-15.6% of volatiles are given off in 1-16 hrs. while the film wt. remains const.; at 150° for 6 hrs., 20.1-30.8% (including 4.5-7.6% of high-boiling matter) are given off and the film loses up to 11.4% of its wt. The drying mechanism of II probably is peroxidic up to 100°, and I-like above 130°. II films at 20, 70, 80, 90, 100, 120, 140, 160, and 180° dry in 5760, 540, 300, 270, 180, 120, 70, 40, and 20 min. resp., indicating a rate which changes with increasing temp. When these films were further exposed to air (at 20°) for 80 weeks, their wt. changes fell from a 10.8% loss to a 1.1% gain with increasing drying temp. The drying balance (change of film wt. plus losses to the atm.) of a II film at 100° is 21.8 to 24.7% (3 hrs.): at 135-40° it is only 8.4-12.9% (3 hrs.); at 135-40° it is only 8.4-12.9% (1 hr.); when heating is continued at 100° for 8 hrs., the balance rises to 46.2-50.5%, while at 135°, for 8 hrs., it remains about the same. Prolonged heating (440-571 hrs. at 160°) did not herm II films except for discoloration and a mex. wt. loss of 30-5%. With increasing temp., the max. wt. increase was shifted further from the dry point, and took longer to reach." From C. A.

Scheifele, B.

GENERAL INTERPRETATION OF THE DRYING PROCESSES OF FATTY OILS. Farben-Ztg. 32, 739-41 (1927); C.A. 22, 3052 (1928). "The drying processes of all drying oils, whether of the tung oil, linseed oil, or poppyseed oil groups, are explained with reference to the relative unsath. of their mols. and consequent tendency to gel formation." From C. A.

Scheifele, B.

A COMPREHENSIVE THEORY OF THE DRYING PROCESS AND OF THE HEAT POLYMERIZATION OF FATTY OILS.

Z. angew. Chem. 42, 787-90 (1929); C.A. 23, 5050 (1929).

"The drying of an oil depends on the no. and position of the double bonds in the fatty acid radical. Conjugated double bonds greatly increase the rate of drying or polymerization. The behaviors of china wood, linseed and poppyseed ails are explained on this basis. Objection has been made that butadiene should be at least as good a drying oil as china wood oil since it contains conjugated double bonds. S. replies that butadiene does polymerize to rubber-like substances but the mol. is too small to be classed with the ordinary drying oils." From C. A.

Schmidt, Walter

THE DRYING PROCESS OF CHINESE WOOD OIL. Farben-Ztg. 29, 1261-2 (1924); C.A. 18, 2968 (1924). "Various samples of tung oil allowed to dry in the light, and in the dark st verying humidities and temps. always dried without gloss, but in a desiccator over $CaCl_2$ they dried clear and exceptionally hard in three weeks. This slow drying period was not accelerated by passing a const. stream of dry air through the desiccator. When the desiccator is open for even short periods such as are required for making weighings, a frosted film is likely to result. Increases in the weights of films in room air and in the desiccator were practically the same. In the absence of moisture, tung oil is apparently a relatively slowly drying oil, while the commonly observed drying probably consist of a colloidal coagulation process with H₂O as flocculating medium. The clear wood oil films which Fahrion obtained by the use of a solution of the oil in Et₂O, may have been due to residual solvent acting in a manner opposite to that of traces of moisture. Graphs are given of the effect of

different film thickness on increase in weight of the film." From C. A.

Scofield, Francis

PHYSICAL PROPERTIES OF OIL FILM. III. FURTHER DATA ON DRYING TIME OF OIL MIXTURES AND SOME NOTES ON DURABILITY. Natl. Paint, Varnish Lacquer Assoc. Circ. <u>522</u>, 295-301 (1936); C.A. <u>31</u>, 1640 (1937).

"Drying time of mixt. of tung, oiticica, fish and perilla oils with soy, hempseed, sofflower and sunflower oils is reported. Tung and oiticica oils increase the durability and shorten the drying time of semidrying oils. Perilla oil is less effective. Fish oil, in amts. up to 50% makes no significant change." From C. A.

Silleck, C. F. and Lauren, S.

SOME OBSERVATIONS ON WRINKLE FINISHES.

Notl. Paint Bull. 7, (12), 5-8, 12-13 (1943); C.A. 38, 1129 (1944).
"An attempt to review and supplement the literature on the formulation of wrinkle enamels from the standpoint of texture control.
Factors involved in control of wrinkle texture, compn. of the wrinkle enamel, processing of the wrinkle enamel and application of these enamels are considered." From C. A. Describes wrinkling of tung oil.

Singer, R.J.R.

PHOTCELASTIC EXAMINATION OF FILMS OF OII VARNISHES AND OF STANDOILS. Congr. tech. intern. ind. peintures inds. assoc. 1, 192-202 (1947) (in French)*; C.A. 43, 8701 (1949).

"The behavior under stress, max. elongation, breaking strength, and the specific birefringence m_{SP}, resulting from strain, were studied on free films of standoils (I) and of varnishes (II). (1) The films were held between a fixed jaw clamp and another which replaced the right pan of a beam scale, and wt. was added to the left pan. Changes in length and width of the films were measured; through them, a beam of monochromatic Na light, polarized to 45° with the direction of stress, was passed and its deviation measured in a Berek compensator. (2) The optical devices were combined with a Schepper tester. (3) Difficulties with these devices were eliminated by the use of a spring dynamometer in which the film was stretched within a rigid frame with a spring supplying the stress. Films were

prepd. by casting or spraying on glue-coated paper, drying them 3-8 days, removing the support by washing with cold water, conditioning, and cutting into strips. Films of linseed oil I (no. 50 poises; 0.3% Pb, 0.05 Mn, 0.02 Co as naphthenates) were extended 0.875% per g./sq. mm. of stress; when aged 24 hrs. at 180°, this fell to 0.675%; their msp. rose 0.85 mµ per g./sq. mm. of stress (photoelastic coeff.), but 1.12 mµ after aging. The films broke at 36% extension and 40 g./sq. mm. stress, and at 27% and 40 g./mm. after aging. The aged films showed greater m Films of II made from Super-Beckacite 1001 (alkyl phenol-CHo0 resin), raw china wood oil, and linseed oil I in the ratio 1/2.25/2.25 (A) and 1/1.1/1.1 (B), and from Albertol 111 L (a rosin-modified PhOH-CH,O resin), china wood oil I, and linseed oil I in the ratio 1/1.1/1.1 (C) and 1/0.4/0.4 (D), showed the following max. % elongation, breaking strength (g./sq. mm.), and max. m_{sp} (mµ), resp.: A, 139.5, 238, 120; B, 138, 140, 100; C, 120, 320, 76; D, 108, 280, 67. After aging 24 hrs. at 80°, the values were: A, 119, 160, 40; B, 117, 320, 53; C, 110, 420, 45; D, 102, 240, 30." From C. A. (sbridged)

Stern, E.

NEW STUDIES IN THE PHOTOMICROGRAPHY OF PAINT FILMS. Farben-Ztg. <u>35</u>, 560-3 (1929)*; C.A. <u>24</u>, 736 (1930). "Linseed oil, vulcanized hot or cold with S or S₂Cl₂ approaches tung oil in its water resistance. Photomicrographs of various types of films which have been immersed in water are given. The greater the water absorption, the more prominent is the sepn. of a film into 2 phases." From C. A.

Sward, G. G.

FROSTING OF TUNG OIL.

Natl. Paint, Varnish Lacquer Assoc. Circ. <u>481</u>, 168 (1935); C.A. <u>30</u>, 7881 (1936).

"Frosting and wrinkling of films contg. tung oil is not prevented by 4% of 'Mittel,' believed to contain rosin or a phenolic resin." From C. A.

Sward, G. G. and Gardner, H. A.

CONSTITUTION AND DRYING OF TUNG OIL.

Am .: Paint Varnish Mfrs.: Assoc.Sci.SectCirc. <u>358</u>, 58-62 (1930); Brit. Chem. Abstracts <u>1930</u>, B, 620.

"A brief resume of the present knowledge of the structure of tung oil." From Brit. Chem. Abstracts.

Thomas, C.A., and Marling, P. E.

DRYING RATES OF SYNTHETIC RESINS WITH DRYING OILS. I. CHINA WOOD OIL. Ind. Eng. Chem. 24, 871-3 (1932); C.A. 26 4967-8 (1932).

" β -Naphthel accelerates the drying of Chine wood oil with or without metallic driers under most conditions and in general prevents gas checking. PhOH has a similar but much slighter effect. β -Naphthel also generally accelerates the drying of wood-oil varnishes made from neutral, but not acid, resins. The drying of various synthetic-resin wood-oil varnishes, with and without driers and with or without β -naphthel, under a variety of conditions is reported in numerous tables. β -Naphthel has no accelerating effect upon mixts. of wood oil with other oils." From C. A. Tobies, Klaus

THE APPLICABILITY OF TALL OIL INSTEAD OF LINSEED OIL AS A BINDING AGENT FOR PRINTING INKS.

Forben-Ztg. 45, 68-9, 86-7, 117-19, 133-4, 150, 167-8, 183 (1940); C.A. <u>35</u>, 1249-50 (1941).

"O-absorption tests carried out at 20° in a special app. showed that linseed oil and poppyseed oil absorb 0 much faster than does wood oil or the 4 toll oil esters (which absorb 0 more slowly than wood oil) and that the stand oil prepd. from the tall oil glycol ester absorbs O somewhat faster than do stand oils prepd. from tall oil glycerol esters (linseed stand oil absorbs 0 only slightly faster than does the stand oil prepd. from tall oil glycol ester). Based on O-absorption tests at 100° with stand oils (from linseed oil or tall oil glycerol ester prepd. from tall oil contg. 33% rosin) contg. 0.1, 0.25, 0.5 and 0.75% (metal basis) of Co, Mn or Pb naphthenate, resp., Mn is a somewhat superior catalyst to Co, while Pb shows only slight activity. With stand oil (contg. 0.25% of the resp. metal) prepd. from tall oil glycol ester, Mn is much superior to Co as a arier, while Pb shows slight neg. catalytic action. Actual drying tests made with the stand oils (from linseed oil or tall oil glycerol esters) contg. drier and Permanent Red R Extra showed that (1) the Co naphthenate drier gave results comparable with those expected from C-absorption tests while Mn and Pb naphthenates did not and (2) while stand oil from tall oil glycerol ester (prepd. from tall oil having a high rosin content) might be suitable for printing inks, that from tall oil glycol ester is not satisfactory." From C. A.

Ulrich, H.

CRYSTALLIZATION, FROSTING AND GELATION OF TUNG CIL. Farben-Ztg. <u>39</u>, 704-5 (1934); C.A. <u>23</u>, 5688 (1934).

"The eleostearin content of tung oil is responsible for crystn. and frosting of the oil. Insofar as the oil is unpolymerized, the tendencies still prevail. If monoeleostearin is formed by reaction of tung oil with glycerol, or by cooking with other oils or resin acids, the above phenomena also disappears." From C. A.

Van Heuckeroth, A. W.

PHYSICAL PROPERTIES OF OIL FILMS. II. ELASTICITY OF FILMS. Natl. Paint Varnish Lacquer Assoc., Circ. <u>520</u>, 282-9 (1936); C.A. <u>30</u>, 8654 (1936).

"Unsupported films of raw linseed, row perillo and heat-treated tung oils, pigmented with white lead, Zn oxide and TiO₂ were aged for 2,4 and 8 weeks. The set aged 4 weeks was also exposed to a Hg arc for 50 hrs. The films were then given elongations up to 30% in 5% steps and the percentage recovery, elongation at breaking point and tensile strength observed. Results on films of 26 com. house paints are also given." From C. A.

Wilborn, F.

THE DRYING OF TUNG OIL VARNISHES.

Farben-Ztg. <u>34</u>, 2775-6 (1929); C. A. <u>23</u>, 5336 (1929). "Tung oil varnish was caused to dry with a clear film on the one hand and with a mat film on the other. When the films were dry the increases in weight were 8 and 2% respectively. Drying of tung oil films takes place not uniformly but in patches which grow and unite as drying proceeds." From C. A.

Wolff, H.

THE DRYING OF WOOD OIL.

Chem. Umschau 31, 98-9 (1924); C.A. 18, 2614 (1924).

"W. refers to his article to be published in the Farben Ztg. in which he shows that the 'ice flower' formation in dried wood oil is not due to crystn., but to the formation of folds and wrinkles. The appearance of the hardened film of wood oil is exclusively a colloidal phenomenon, induced probably by oxidation products or some other chem. change. W. illustrates this by the changes that have occurred in a thin layer of wood oil between 2 glass plates, the edges of which had been sealed and had been kept for several yrs. protected from light in a box. This prepr. now shows a granular ground mass with numberless microscopic and macroscopic oil droplets which were analyzed after coalesence by gentle tapping, and showed a Br No. of 106 and these figures correspond to unchanged wood oil which had sepd. from the solid phase, a phenomenon typical of 'ageing' and extended syneresis." From C. A.

Wolff, H.

THE DRYING OF TUNG OIL AND ITS SO-CALLED "WEBBING". Farben-Ztg. 29, 1105-7 (1924); C.A. 18, 3729 (1924). This article is similar to "The Drying of Wood Cil" by H. Wolff. Chem. Umschau. 31, 98-9 (1924); C.A. 18, 2614 (1924).

Wolff, H.

NOTE ON THE DRYING OF WOOD OIL.

Farben-Ztg. 34, 2941-2 (1929); C.A. 24, 251 (1930).

"A dried wood-cil film was stored between glass plates in the dark. After 15 months drops of liquid and granular particles were noted. After 12 months more, small crystals (probably β -eleostearin) were observed in the liquid phase." From C. A.

Wolff, H., and Zeidler, G.

WRINKLING OF WOOD-OIL VARNISHES. THE EFFECT OF THE DRIER. Farben-Ztg. 40, 1010 (1935)*; C.A. <u>30</u>, 884-5 (1936).

"The wrinkling of a no. of varnishes, which contained the 'wrinkling'-preventing agent 'Mittel 109 J,' and which were prepd. from various resins and an improperly heat-treated China wood oil, was more severe with a Mn-Pb combination drier than with a Co drier." From C. A. Copolymerization

Adam, N. K., Morrell, R. S., and Samuels, H.

- THE BLCOM OF VARNISH FILMS. II. THE MALEIC ANHYDRIDE CONPOUNDS OF ALPHA- AND BETA-ELEOSTEARIN.
 - J. Soc. Chem. Ind. 53, 260-2T (1934); C. A. 28, 7041 (1934).

"The film contact angles were measured as in Part I. The airdried and some of the stoved β -eleostearin films bloom and have low contact angles, whereas the very slow air-drying a-films have high contact angles and show no bloom. Co, Mn and Pb resinate driers have no effect on the contact angle or blooming of β -films. Esterification of the β -compd. with ethylene oxide or glycerol raises the contact angle, and thus diminishes the water-attractive power. The β -compd. has a double linking nearer to the surface than does the a-compd. It should therefore have its peroxide grouping nearer the surface, and therefore bloom more readily, as observed. The effect of esterification is due to assocn. of neighboring peroxide groups." From C.A.

Armitage, F., and Cottrell, J. A.

CONJUGATED LINFAGES IN THE C/RDON CH/IN AND THEIR ROLE IN THE SURFACE COATING INDUSTRY. III, CONJUGATED RYING OILS.

Paint Technol. 13, 307-8, 311 (1948); C. A. 42, 8489 (1948). "Tung, oiticica, dehydrated castor, and conjugated linseed oils are considered. Reaction products of tung oil with maleic anhydride can be esterified with unsatd. alcs. to yield solventless thermosetting coatings. By conducting the reaction in terpene solvent, tung oil and styrene can be made to react to give useful products." From C. A.

Bhow, N. R., and Payne, H. F.

STYRENE COPOLYMERS IN ALKYD RESINS.

Ind. Eng. Chem. <u>42</u>, 700-3 (1950); J. Am. Oil Chemists' Soc. <u>27</u>, 327 (1950).

"The mass polymerization reaction of styrene with tung, oiticica, and dehydrated castor oils was slowest with tung and fastest with castor. The ketonic group of oiticica is believed to accelerate the reaction and the faster rate with castor is probably due to the disappearance of styrene in forming polystyrene. Alkyd resins from styrenated castor were faster air-drying and baking than medium or short oil alkyds; their films have better chemical resistance." From J. Am. Oil Chemists' Soc.

Blagonravova, A. A., and Karlinskaya, R. S.

LACQUER RESINS FROM MALEIC ANHYDRIDE.

J. Chem. Ind. (U.S.S.R.) <u>18</u> (4), 25-8; (11), 19-21 (1941)*;

C. A. <u>38</u>, 4142 (1944).

"Partly hydrolyzed linseed, sunflower or cottonseed oils contain mixts. of mono- and diglycerides and some free glycerol (I). Such oils react with maleic anhydride (II) to give a dark tar which results from reaction of I and II. To obtain satisfactory plastics, I must be removed, by washing with hot H₂O, or better, by adding enough phthalic anhydride (III) to react

with I but not enough to react with the glycerides. The mixt. is then allowed to react with II to give a phthalomaleic resin. sol. in turpentine or xylene, which can be used for lacquers. The films are very H_O resistant, especially when the content of III is low. When free fatty acids are present, the resins are darker. If the reaction is carried out in BuOH, the resulting resins are much softer, owing to formation of Fu esters which act as plasticizers. Ibid. No. 11, 19-21 (1941), -- When 5-25% maleic anhydride (I) is added to tung, linseed, sunflower, cottonseed or olive oil at 180-200°, it gives a light colored resin with lowered acid and I no. If more than 25% I is used, the soly. of the product is lowered. The viscosity of the product depends on the amt. of I used and the length of heating. In tung oil, I unites with a double bond which does not add I, and so the I no. of the product falls only if the product is polymerized. The residual free acid groups can be esterified with ethylene glycol, and glycerol can be " used if the product contains less than 10° I. CaO can also be used to neutralize the acidity. The resins can be used in lacquers, but those prepd. from semidrving oils are satisfactory only for hot drying." From C. A.

Brunner, H., and Tucker, D. R.

NATURE OF PRODUCTS OBTAINED BY REFLUXING STYREME AND DRYING OILS IN XYLENE SOLUTION.

Research (London) 2, 42-6 (1949)*; C. A. 43, 4027-8 (1949).

"The reaction products obtained by refluxing mixts. of styrene, drying oil, and xylene without a polymerization agent at 140° have been studied to det. if interpolymerization occurred. Considerable copolymerization took place between styrene and tung oil, but styrene and dehydrated **cas**tor oil undergo no appreciable copolymerization, yielding instead substantial amts. of oil-sol. polystyrene." From C. A.

Earhart, K. A.

THEORIES AND FACTS CONCERNING ALKYDS.

Ind. Eng. Chem. 41, 716-25 (1949); C. A. 43, 5993 (1949).

"Discussions of theoretical compn. of alkyd resins with varying molar ratio of glycerol to phthalic anhydride to fatty acids. The actual manuf. of these resins indicates that practical resins cannot be formulated on the basis of concepts fashioned around theoretical values. When fatty acids are calcd. to triglyceride and mole ratios of glycerol to phthalic anhydride are closely calcd. for oil length of the resin, more practical results are obtained. The use of phthalic anhydride content as a measure of durability is not dependable, as resins of the same analysis may differ sharply on exposure. The effect of various oils and the amt. of oil modification of the resin, with resultant properties, is covered thoroughly, as are the properties of polyfunctional acids and polyhydric alc. used in modern resin manuf. Equations for the kinetics involved in reactions, graphs depicting the reduction and a discussion of the compatability, stability, and wetting power of alkyd resins complete the examn. of the factual and theoretical concepts of alkyd resins." From C. A.

Gee, Geoffrey.

REACTIONS IN MONOLAYING OF DRYING OILS. II. POLYMERIZATION OF OXIDIZED FORMS OF THE MALEIC ANHYDRID'S COMPOUND OF BETA-ELEOSTEARINE.

Proc. Roy. Soc. (London) <u>A153</u>, 129-41 (1935)*; Trans. Faraday Soc. <u>32</u>, 187-95 (1936); C. A. <u>30</u>, 2025 (1936).

"Analysis showed that the polymerization is a chain reaction which can be broken by inhibitors like hydroquinone in the substrate or like Et myristate in the film itself. By compressing a film that had been oxidized at high pressure, polymerization of the stable isomer was studied. k varied directly with the 3rd power of the pressure as in Semenoff's equation for gaseous chain reactions, and the energy of activation was 20,000 cal./mol. Polymerization of the unstable peroxide was studied at temps. at which reaction of the isomer was negligible. Pressure and temp. had a marked effect on this polymerization, and the stable isomer acted as inhibitor. The energy of activation was 5000 cal./mol." From C. A.

Gee, Geoffrey.

STUDIES IN THE AUTOXIDATION OF MONOLAYERS. II. CATALYSTS AND INHIBITORS.

J. Chem. Fhys. <u>5</u>, 801-7 (1937); C. A. <u>31</u>, 8316 (1937). "The effect of the catalysts $CoSO_1$, $FnSO_4$, $Pb(OAc)_2$, iodoacericacia, p-nitraniline, piperidine and hydroquinone in the substrate on the rate of oxidation of monolayers of maleic anhydride-a-eleostearin was detd. The direction and magnitude of the catalytic effect depend on the pH of the substrate. A semiquant. kinetic treatment accounts for the principal features of the results." From C. A.

Gee, G., and Rideal, E. K.

STUDIES IN THE AUTOMIDATION OF MONOLAYERS. I. THE NECHAMISM OF AUTOMIDATION OF MALEIC ANHYDRIDE BETA-ELEOSTEARIN.

J. Chem. Phy. <u>5</u>, 794-801 (1937); C. A. <u>31</u>, 8316 (1937). "The autoxidation of monolayers of maleic anhydride β-eleostearin was detd. at 8 and 10 dynes, 4° and 17°, and pH 0.7 to +12.0; a free radical mechanism is proposed." From C. A.

Masereel, G.

PROPERTIES AND AFTLIC/TION FOSSIBILITIES OF STYRENEATED OILS. Chim. peintures 12, 206-8 (1949).

Styrene has been added to drying oils (linseed, wood, oiticica, dehydrated castor, soybean, etc.) to produce more or less viscous materials suitable for use in the manufacture of varnishes and paints. Styrenated oils are noted for drying rapidly without wrinkling, good spreadability, and great durability. Morrell, R. S., and Davis, W. R.

STUDIES IN THE CHIDATION OF DRYING OILS AND COGNATE SUBSTANCES. II. (A) THE OXIDATION OF THE MALEIC ANPYDRIDE COMPOUND OF ALPHA-ELEOSTEARIC ACID. (B) FURTHER STUDIES IN THE PROPERTIES OF MALEIC ANHYDRIDE CONFOUNDS OF ALPHA- AND BETA-ELEOSTETRIC ACIDS.

J. Soc. Chem. Ind. 55, 261-5T (1936); C. A. 30, 8654 (1936).

"The maleic anhydride addn. compd. of eleostearic acid (cf. 0. A. 26, 5545) absorbed 2 atoms of 0 in AcOH at 20° in the presence of $Co(OAc)_2$. Oxidation was much slower than for the corresponding β -derivative. The oily product, contg. little peroxide or polymer, gave no azelaic acid on ozonization. The structure is concluded from this and from analysis, I no., and Zerewitinoff detn. to be

 $CH_3(CH_2)_3CH.CH.CH.CHCOCH(OH)(CH_2)_7COOH$

Comparison with the corresponding β -deriv., which forms peroxide and polymerizes readily, indicates that only "remote" ethanoid linkages are concerned in the drying process. The maleic anhydride compds. of α - and β -eleostearic acids were hydrogenated (PtO₂) to the tetrahydro α -compound (C₂₂H₃₆O₅), m. 74°, and the tetrahydro α -compound (C₂₂H₃₆O₅), m. 74°, and the tetrahydro α -compd., m. 63°. The maleic anhydride compds. of β - and β -eleostearins absorbed theoretical atts. of H but products did not crystallize. The malcic anhydride compds. with 30% H₂O₂ in ACOH gave noncryst. dihydroxy derivs."From C.A.

Morrell, R. S., and Davis, W. R.

STUDIES IN THE QXIDATION OF DRYING OILS AND COGNATE SUBSTANCES. III. EFFECT OF HEAT ON THE OXIDIZED BETA-ELEOSTEARIN-MALEIC ANHYDRIDE COMPOUND.

J. Soc. Chem. Ind. <u>55</u>, 265-7T (1936); C. A. <u>30</u>, 8654 (1936). "The oxidized maleic anhydride β-eleostearic acid product, polymerized in AcOH ("a true polymeride in which primary valence acting at the peroxide grouping links mol. to mol.") lost its small peroxide value at 100° and did not depolymerize. The gel polymer formed in CCL, and having the theoretical peroxide value, the mols. being held together by secondary valence forces, lost all its peroxide value at 100° and increased in C percentage. The main reaction is believed to be:

CH.CH.O.O. CH.CH.O." From C.A.

Morrell, R. S., and Davis, W. R.

STUDIES IN THE OXIDATION OF DRYING OILS AND COGNATE SUBSTANCES.
I. THE OXIDATION OF THE MALEIC ANHYDRIDE COMPOUNDS OF BETA-ELEOSTEARIC ACID AND ITS TRIGLYCURIDE."
J. Soc. Chem. Ind. <u>55</u>, 237-46T (1936); C. A. <u>30</u>, 8654 (1936). This article is similar to "Drying Oils and Related Unsaturated Compounds" by Morrell and Davis, Trans. Faraday Soc. <u>32</u>, 209-19 (1936); C. A. <u>30</u>, 2777 (1936). Northwestern Paint and Varnish Production Club.

TALL-OIL VARNISHES.

Official Digest Federation Paint Varnish Production Clubs No. 286, 845-53 (1948); Paint, Oil Chem. Rev. <u>111</u> (23), 42, 44-6 (1948).

A series of tall-oil esters are prepd. with glycerol, pentaerythritol, dipentaerythrytol, and other polyhydric alc. with and without dibasic acids. One series was made with styrene, and a control with a pentaerythritol rosin ester varnish of half tung, half soya oil. The esterification procedure, time, and temp. are given, with data on varnishes, enamels, and barn paints made from the esters. Cost figures, phys. data, and accelerated test results are listed.

Peterson, Norman R.

STYREMATED OILS.

Am. Paint J. <u>32</u> (40), 32, 34, 37-8, 40 (1948); Can. Paint & Varnish Mag. <u>22</u> (12), 34, 36-7, 47-8 (1948); C. A. <u>42</u>, 6132-3 (1948); <u>43</u>, 1577 (1949).

"Oil-sol. phenolic resins, alkyd resins and nitrocellulose are the 3 major classes of synthetic film formers developed during the past 25 yrs. Styrene is rapidly developing into the 4th major synthetic coating material. Methods have been worked out for making styrene react with all varieties of drying oils to produce products that are: fast drying, light colored, durable at any reasonable viscosity, and have good water and chem. resistance, good elec. properties, and low cost." From C.A.

Styrone reacts so rapidly with tung oil that blending tung with soybean or similar oil is desirable. Conjugated drying oils are considered as substituted but dienes with styrene adding by 1:4 addition.

Pickett, C. F.

CIL-SOLUBLE, UNMODIFIED "HENCL-FORMALD HYDE RESING, REACTIVE AND NON-REACTIVE.

Official Digest Federation Paint & Varnish Production Clubs No. 156, 185-9 (May 1936); C. A. 30, 5434-35 (1936).

"Amberol ST-137 (I), a reactive resin, and Amberol ST-137-X (II), a nonreactive resin, were made into 50-, 30-, and 15-gallon varnishes by using tung oil with 105 linseed oil, except for the 15-gallon varnishes, which were 100% tung oil. I is paler with less after-yellowing. II is more gas-proof, more alkali-resistant, and more durable, especially for the varnishes of lower oil content. Mn and Co aid in keeping the lead drier in soln." From C. A.

Schroeder, H. M., and Terrill, R. L.

STYRENATED DRYING OILS.

J. Am. Oil Chemists' Soc. <u>26</u>, 153-57 (1949); C. A. <u>43</u>, 4871 (1949). "Styrenated oils were made from refined linseed, soybean and also from the oxidized oils, from mixts. of 10 to 20% tung oil with the refined oils, and from dehydrated and oxidized castor oil by mixing with 45% styrene and 3% benzoyl peroxide, based on wt. of styrene, and heating up to 21 hrs. at 250 and 300°. The reaction is rapid for 2 or 3 hrs. and then slows down. The color of the product is generally light and it is highly viscous or a semisolid resinous material and its properties vary with the type of cil used. The product is comparable to those of oleoresinous vernishes and alkyd resins where the copolymerization is carried out with oils known to contain large amts. of conjugated systems. The set is rapid and hard and the material has excellent water and alkali resistance." From C. A.

Teeter, H. M., Scholfield, C. R., and Cowan, J. C.

REACTIONS OF CONJUGATED FAT ACIDS. I. ADDITION OF CROTONIC ACID DURIV TIVES.

Oil & Soap 23, 216-19 (1946); C. A. 40, 5268 (1946). "Addn. products of ethyl crotonate and crotononitrile with conjugated methyl linoleate (I), derived from soybean methyl esters and conjugated with a Ni-C catalyst were prepd. The addn. product of ethyl crotonate and non-conjugated I was prepd. and compared with that from conjugated I. The addn. product of ethyl crotonate and conjugated I was sapond. to a dibasic acid which was used to prepare a decamethylene glycol polyester and an ethylenediamine polyamide. The compatability of the addn. product of ethyl crotonate and conjugated I with various synthetic resins was detd. 27 references." From C. A.

Reference is made to the reactions of maleic anhydride with eleostearic acid and its glyceride.

Other Reactions

Anonymous

REDUCTION OF ESTARS OF FATTY ACIDS BY SODIUM. Bull. mens. ITERG No. 9, 3-9 (Aug.-Sept., 1947) (in French). This is a review containing much information similar to that in "Sodium Reduction of Fatty Acid Esters," by V. L. Hansley, Ind. Eng. Chem. 39, 55-56 (1947).

Armitage, F., and Cottrell, J. A.

CONJUGATED LINKAGES AND THEIR NOLE IN THE SURF'CE-COATINGS INDUSTRY.

Paint Technol. 12, 426-8 (1947); C. A. 42, 3588-9 (1948).

"A review of structures, types of unsatn., and theories of the reactions of double bonds." From C. A.

It is to these reactions of conjugated linkages that tung oil owes its properties of rapid polymerization and drying. Balaty, V. F., Fellinger, L. L., and Audrieth, L. F.

ACID CAT.LYSIS IN LIQUID AMMONIA. AMMONOLYSIS OF FATTY OILS. Ind. Eng. Chem. <u>31</u>, 280-2 (1939); C. A. <u>33</u>, 4807 (1939).

"The anmonolysis of natural oils and fats by the action of liquid NH₃ to produce mixts. of fatty acid amides is catalyzed by NH₄ salts. Solvolytic reactions of this type represent a special case of acid catalysis in a nonaq. solvent. Amide mixts. were prepd. from olive, cottonseed, maize, soybean, castor, linseed, perilla and tung oils, and from pork lard. Five g. oil was shaken in a sealed Pyrex tube with NH₂ made up to 25 cc., at 25° and 165°, for periods up to 164 hr. The N contents and I nos. of all ammonolyzates were detd. Both were low in tung and linseed oils." From C. A.

Bauer, K. H., and Hugel, F.

POLYMERIZED PERILLA OIL.

Chem. Unschau Fette, Oele, Wachse. u. Harze 32, 13-7 (1925); C. A. 19, 1501 (1925).

"A polymerized perilla oil, viscous, insol. in alc., sol. in ether, xylene and CHCl₃, I no. 80.6 (Hanus), was sapond. The liberated acids had acid no. 113.5 and I no. 89.1. Oxidation of the acids by 2% KMnO, soln. followed by extn. with petroleum ether and ether, showed in the ether residue acid no. of 113,6, I no. of 33.9, acetyl no. of 129.9 and a mean mol. wt. of 447.4 by Rast's camphor method. No H2O-sol. oxidation products were obtained, while fresh perilla oil yields H₂O-sol. linusinic and iso-linusinic acids as oxidation products of its linolenic acid. Hydrogenation of the acids yielded mainly stearic acid. The original polymerized oil was then extd. with acetone, and both the sol. and insol. portions were saponified, and the acids liberated, which then showed the following consts. for the portions sol. and insol. in acetone, resp.; I no. 86.9, 80.8; acid no. 185.0, 204.6; mean mol. wt. in benzene 422,1, 820; mean mol. wt. in camphor 214.6, 408; On hydrogenation both portions yielded stearic acid. On oxidation with KMnO1 both produced dihydroxystearic acid, but the acetone-sol. portion in addition gave some oily H2O-sol. acids of low mol. wt. while the acctone-insol. portion showed in the filtrates a substance with acid no. 383.3. Oleic acid had apparently remained unchanged during polymerization, the linolic and linolenic acid lose their I no. while eleostearic acid increases its mol. wt. The camphor soln. for the detg. mol. wt. gives results that show only 1/2 the value of that in benzene solution. The gelatinization of wood oil shows the characteristics of a colloidal chemical change." From C. A.

Bauer, K. H., and Herberts, K.

INVESTIGATIONS ON CHINA WOOD OIL.

Chem. Umschau Fette, Oele, Wachse u. Harze <u>29</u>, 229-32 (1922); C. A. <u>16</u>, 3550 (1922).

"Chinese wood oil contains principally a-elaeostearic acid and a small amt, of oleic acid. It is isomeric with linolic acid, contg. 2 double bonds, m. 48° and easily changes to β -elaeostearic acid, m. 71°, Other investigators have shown its most probable formula to be CH3(CH2)2CH:CH.CH2CH2CH:CH(CH2)7COOH while linelic acid has the formula CH3(CH2), CH:CH:CH2CH:CH. (CH2)7 COOH[Sic]; thus the tetrabromide of these 2 acids should not be the same although they have the same m.p. B. and H. now show that the tetrabromide of a-elaeostearic acid yields by debramination of its alc. soln. by Zn dust the β -variety, m. 71°; this confirms Nicolet's opinion that the tetrabromide of elaecstearic acid is not identical with that of linolic acid. The methyl ester of the a-acid yielded the β -acid on sapon. while the anhydride of the e-acid gave the e-acid on sapon. again." From C. A.

Bauer, K. H., and Rohrback, E.

THE HEXIBROMIDE OF ELEOSTEARIC ACID.

Chem. Unschau Fette, Oele, Wachse u, Harze 35, 53-4 (1928); C. A. 22, 2073 (1928).

"Eighteen g. a-eleostearic acid in 180 g. petroleum ether in a freezing mixt. was exposed in a quartz flask to ultra-violet light and Br added dropwise with agitation to the amt. of 6 atoms Br; a white solid sepd. after several hrs. with evolution of much HBr. Recrystd., it sinters at 134° and m. 139-141°; it is sol. in $C_{6}H_6$, Me₂CO, CHCl₃ and ether; less so in alc., ligroin and AcOEt. Analysis confirms the formula $C_{18}H_{30}O_2$ Br₆. By debrominating with Zn in alc. the β -eleostearic acid, m. 69-71°, was obtained. An oily by-product of the hexabromide has a Br content between that of penta- and hexabromide, and when debrominated with Zn in alc. it yields an oil with a Br content between di- and tribromoeleostearic acid." From C. A.

Bauer, W. W.

SOME DEVELOPMENTS CONTROLLING CHINA WOOD OIL VARNISHES. Ind. Eng. Chen. 18, 1249-51 (1926); C. A. 21, 659 (1927).

"China wood oil pressed at high pressures from meats contg. high per cents of inner shells has formed a solid modification out of contact with light. China wood oil crystn. has been produced in the absence of light. Evidence is offered to show this to be due to rapid absorption of 0 and formation of surface gel. A method for measuring the tendency of China wood oil varnishes to crystallize is described." From C. A.

•

Biltz, K., and Simon, W.

STUDIES OF HIGHLY OXIDIZABLE OIL TREATED TO RETARD IGNITION. Monatschr. Textil-Ind. 56, 185-8 (1941)*; Chem. Zentr. 1942, I, 554; C. ... 37, 2602 (1943).

"The effects of addns. of α - and β -naphthol and of pyrocatechol on the spontaneous ignition of linseed oil, sunflower oil, tung oil, sunflower-oil fat acids and tall-oil fat acids were detd. Pyrocatechol exerts the max. action in all cases; however, tung oil cannot be protected sufficiently even by the use of this compd. β -Naphthol is the least effective." From C. A.

Böcseken, J.

RESEARCHES ON VEGETABLE OILS IN THE CHEMICAL LABORATORY OF THE TECHNICAL UNIVERSITY OF DELFT.

Congr. intern. tech. chim. ind. agr., Conpt. rend. V^e Congr. 2, 348-66 (1937); C. A. <u>32</u>, 3647 (1938).

"General discussion of about 15 years work with 57 citations. Subjects studied were sp. gr., distn. at high vacuum, I no., oxidation and drying of unsatd. oils, behavior of conjugated double bonds, and isolation and study of minor constituents e.g. biacetyl in butter and sesamin in sesame oil." From C. A.

Constants are reported for α - and β -eleostearic acids, β -eleostearin and ethyl α -eleostearate.

Bocseken, J., and Krimpen, J. van.

THE REDUCTION OF ALPHA-ELEOSTEARIC ACID; 10, 12-LINOLEIC ACID AND THE 11-OLEIC ACID.

Verslag. Akad. Wetenschappen Amsterdam 37, 66-8 (1928); C. A. 22, 1953 (1928).

"a-eleostoaric acid, $Me(GH_2)_7 GH: CHCH: CHCH: CH(CH_2)_3 CO_2H$, m. 46°, b. 159-70.5°, n_D^{15} 1.5043-1.5086, has been esterified; the Et ester has been distd. in a cathodic vacuum and hydrogenated with only 1 mol. H₂. The resulting ester has a mol. refraction = 96.87, indicating an exaltation of 1.59 due to 1 pair of conjugated double bonds. The free acid, m. 28.5°, n^{7O} 1.4639, obtained therefrom, has 2 double bonds, in the 10,^D11- and 12, 13-positions, this being ascertained by ozonization. A further reduction gives an 11-ethylene acid, m. 52-3°, which seems to be identical with vaccinic acid (cf. Bertram, C. A. 21, 2391)." From C. A.

Boeseken, J., and Krimpen, J. van.

THE REDUCTION OF ALPHA-ELEOSTEARIC ACID. (THE LINOLEIC ACIDS-10, 12 AND THE OLEIC ACID-11).

Proc. Acad. Sci. Amsterdam <u>31</u>, 238-240 (1928); C. A. <u>22</u>, 2551 (1928).

. A translation of an article by the same authors in Verslag. Akad. . Wetenschappen Amsterdam 37, 66-8 (1928). Cloez, S. M.

THE FATTY MATTER OF THE SEEDS OF THE OIL TREE OF CHINA. Compt. rend. 81, 469-72 (1875); Bull. Soc. Chem. 26, 286 (1876); Chem. Zentr., <u>1875</u>, 690; Chim. News <u>32</u>, 179 (1875). From Elaeococca vernicia (Tong-Yeou or Oil Tree of China) obtained from China can be pressed or extracted with ether a colorless, almost tasteless oil having a d¹⁵ of 0.9362 and which thickens at -18° C. without crystallizing. Extraction with CS₂ yields a crystalline product of m.p. 34°. This solidification was proven not to be caused by heat alone but to be accelerated by light. Saponification of the oil yielded a mixture of acids, one of which formed rhomboidal plates, of m.p. 44° C. The latter became resinous on contact with the air. A Pb soap melts below 100° and is largely soluble in ether. After saponification there was obtained from the water a sirup-like liquid resembling glycerine but possessing a very bitter and disagreeable odor.

Croxford, J. W.

THE DIFFERENTIAL H.LOGEN ABSORPTIONS OF OILS AND FATS. Analyst, <u>54</u>, 445-53 (1929); C. A. <u>23</u>, 4837 (1929). The Cl, Br and I absorbed by tung oil, eleostearic acid, and 23 other oils and acids were determined by Br-vapor and Wijs methods.

Dalton, J.

MYSTERY OF TUNG OIL SOLIDIFICATION. China Trade Monthly 2, 451, 480 (May, 1948).

Deckert, H.

POLYMERIZATION AND ISOMERIZATION OF TUNG OIL.

Farbe u. Lack 1931, 307-8; C. A. 25, 4722 (1931).

"The rate of formation of β -eleostearin in irradiated tung oil is inversely proportional to the time, finally becoming O. If the product be removed at equil. succeeding crops will form in shorter periods. However, the actual amt. of each succeeding crop becomes less. Refining with earth accelerates and cooking retards the formation of β -eleostearin. The rapidity of gelling of tung oil is inversely propertional to the temp. Large amts, of drier favor non-frosting of tung oil films, but introduce other undesirable features." From C. A.

Demmler, P. E.

HARDEVING OF TUNG OIL BY ANHYDROUS FERRIC CHLORIDE SOLUTION. Natl. Research Council, Div. Eng. and Ind. Research, Ann. Rept. Conf. on Elec. Insulation <u>1948</u>, 58-60 (1949); C. A. <u>43</u>, 5605 (1949). "Anhyd. FoCl₃ is dissolved in tritolyl phosphate and the soln. mixed with castor oil which retards gelling. The final mixt. contains about 0.8 wt. % FeCl₃, but the amount is not critical. Thorough mixing is necessary to avoid elec. leakage through the FeCl₃ soln. Gelling occurs in 1.5 min. at 50°, 60 min. at 25°, and takes more than 24 hrs. at 10°. The insulation resistance at 25° increases from about 150 megohms/cc. after mixing to a near-max. value of 2 x 10^5 megohms after 48 days. Curing for 6 hrs. at 70-80° has the same aging effect. The insulation resistance doubles approx. for each 10° decrease." From C. A.

Eibner, A.

THE YELLO ING OF OIL FILMS AND ITS PREVENTION. III. Paint Varnish Production Mgr. <u>14</u>, 7-8, 10-11 (Feb., 1936); C. A. <u>30</u>, 2410 (1936).

"A discussion of Hantz' hypotheses of pseudo acids, as applied to the yellowing oil, and of other hypotheses. The glycerol radical tends to prevent the yellowing of oil films exposed to light. Et ester and glycol esters yellowed in 30 days or less, while the glyceride showed no yellowing after 45 days exposure to light. A decrease of the O content of the films decreases the yellowing tendency." From C. A.

Practical experience has shown that wood oil films yellow more rapidly and to a greater extent than linseed oil films. This raises the question whether in the wood oil molecule the presence of one keto group adjacent to a double linkage could act as a chromophor and cause color.

Eibner, A., Merz, O., and Munzert, H.

CHINESE WOOD OIL.

Chem. Umschau Fette, Oele, Wachse. u. Harze <u>31</u>, 69-82 (1924); C. A. 18, 3728 (1924).

"Five oils of different origins and ages were investigated but most of the detns. were made on an oil of the following consts .: acid no. 3.82, sapon. no. 193.10, I no. 146.2 and sp. gr. 0.941. A quant. sepn. into satd. and unsatd. acids was unsuccessful because both the α - and β -eleostearic acids form Pb salts difficulty sol. in Et_O, so that the "setd." acids obtained showed an I no. of 117,1 and 89.2, resp. A sepn. by Facchini-Doria's method by means of K salts likewise yielded solid acids of 161.1 I no. While eleostearic acid permits of 12 stereoisomers only CH₃(CH₂)₃CH:CH(CH₂)₂CH:CH(CH₂)₇COOH occurs in the oil. It shows 2 methylene groups massed between its 2 double bonds in distinction from linolic acid, which shows only one methylene group between the 8, 9 and 11, 12 double bonds. The massing of the 2 methylene groups between the double bonds gives to wood oil its unusual qualities. The liquid a -eleostearic glyceride of the oil easily isomerizes to the solid β -glyceride under the influence of light, the speed depending upon intensity, length of time and thickness of glass and oil layer. The crude \$-glyceride m. 32°, but when recrystd. from acctone, it m. 60-61°; the free β -acid m. 72 degrees. Drying tests with the solid β -glyceride showed only a slight difference between it and the original oil; the change, therefore, of the ainto the β -glyccride has little, if any, influence upon the

character of the final film. But the free a-acid prepd. by fractional crystn. from alc. at O degree with a m. p. of 48° has somewhat, better drying qualities than the β -acid (m. 72 degree) which difference was accentuated under brown glass, . The change of α -into β -acid by means of Br was studied by mixing the tetrabromide of the β -acid (m. 114°) in varying proportions with the bromide of the a-acid (Nicolet's method) and noting any lowering in the m.p.; the fact that none occurred shows that the isomeric change takes place during bromination and not during the later debromination. The clouding of wood-oil films during drying was followed by the microscope in a series of expts. under varying conditions of light. The cause of turbidity in the dried films is the rapid O2 absorption by the a -eleostearic glyceride, accompanied by unequal vol. changes which produce macroscopic and microscopic folds and wrinkles with diffuse refraction of light. Prevention of cloudy drying is now practically accomplished in manufg. processes. The dried film of wood oil, tungoxyn, is sol, in boiling aniline and nitrobenzene, partly sol. in tetralin and anyl alc. By extg. the films with a mixt. of abs. alc. and ether their acidity was compared with that of linseed and poppyseed oil; after 127 days wood-oil films had an acid no. (59.76) as high as that of linseed oil after 7 days and of poppyseed oil after 12 days. The absence of polymerization was demonstrated in a six-months-old film by extn. with CHCl, and ether and making mol. wt. detns. of the acids of its insol. residue. The wts. found ranged from 122.77 to 217.56, while the actual mol. wt is 266.3. These results indicate mol. splitting rather than polymerization." From C. A.

Eibner, A., and Hunzert, H.

OXYNS. IV. STANDARDIZING OIL COLOR BINDERS. AUTOXIDATION. Chem. Umschau Fette, Oele, Wachse. u. Harze <u>34</u>, 89-96, 101-8 (1927); C. A. 21, 2071 (1927).

"The normal requirements for drying oils comprise rapid drying, permanence of tint, smallest vol. change, hardness of film, soly. in diluents, absence of wrinkles or cracks, etc. The nearest standard is Chinese wood oil, contg. a single acid with 3 double bonds, while linseed oil contains many acids and cellulose lacquers none. A linseed oil film in direct sunlight can lose in wt. as much as a poppy seed oil film and, like it, may re-soften so that standard tests should be made in diffused daylight. Since moist air causes much H₀O absorption and swelling in films and dry air a loss, comparative tests should be made at normal sath. The process of drying involves absorption of O_o, of chemically combined and physically held H20, loss of volatile oxidation products and the presence of positive and negative catalysts. The acid no. of a dry wood oil film was found at 59.76 after 127 days, of a linseed oil film at 185.9 after 2 years, and of a poppy seed oil film at 221 after 127 days. A case of 2 Bombay linseed oils is mentioned which had thickened after standing bottled for 12 years at room

temp. in diffused daylight, showing a mol. wt. of 1714 and 1765, while 50 other samples from all parts of the world and stored in like manner did not show such polymerization. Two "uviol" oils (oils treated with ultra-violet light) had gelatinized throughout their body after standing in the dark for several months, their acetyl no. rising from the original 1.5 and 2.8 to 60.7 and 71.39 and their hexabromide no. dropping from the original 51.5 to 15.8 and 9.6; their gasoline-insol. hydroxy acids had increased from 0 to 42.8. The low acetyl no. of normal films shows the presence of only small amts. of hydroxy acids, while their resistance toward reducing agents and absence of notable peroxides indicate polymerization. All fresh oils and fats yield light-colored soaps while all oxidized or partly oxidized oils give dark-colored scaps, so that the dark color of the scaps of dry oil films is evidence of autoxidation. This color is not due to K or Na, since sapon. in H₀O alone (in closed tube) produces the same dark color. By esterizing the brown acids of an oil film with trichlorohydrin via the Ag salt, the resulting ester is light-colored, showing that only free acids are dark-colored while combined acids are light-colored. The brown color is probably due to a mixt. of oxidation products, that of a -linolenic acid being dark, that of a-linolic acid light and that of oleic acid least colored; pine seed oils also yield dark colors, probably due to β -linolenic acid. The theory of stepwise and limited hydrolysis is incorrect, likewise the theory of an exclusively colloidal reaction. The glycerides are not broken down during drying to free glycerol. Chinese wood oil films also furnish dark-colored acids, and their methyl esters are a dark brown liquid. An attempt to sep. from these esters the free hydroxyeleostearic acid by fractional vacuum distn. failed, only stearic and palmitic acid being found in the distn. The residue from the distn. contained a dark-colored benzene-insol, portion whose analysis came nearest to that of the oxyn of eleostearic methyl ester; its liberated acid could not be reduced nor crystd. and its acetyl no. was low. The general conclusion is reached that the glycerol radical as well as the unsatd. acids are carriers of the drying ability of oils and that glycerol is the only alc. that can form colorless esters with the oxyn acids of dried films." From C. A.

Eibner, A., and Schwaiger, Jos.

CHINESE WOOD OIL. II.

Chem. Umschau Fette, Oele, Wachse. u. Harze <u>33</u>, 77-85 (1926); C. A. 20, 2911 (1926).

"The older view that wood oil contains an a-eleostearic acid with $2CH_2$ groups between the 2 double bonds, $CH_3(CH_2)_3CH:CH(CH_2)_2CH:CH$ "

 $(CH_2)_7$ COOH, is now questioned since J. Boeseken and J. H. Ravenswaay found by refractometric methods that there are 3 double bonds in the mol. An attempt to synthesize the normal *e*-eleostearic glyceride from its acid and glycerol in a CO₂ atmm. and closed tube failed

because at 90° the reaction does not take place and at 110° the mass gelatinized. A 15-yr.-old Hankow oil and a fresh Canton wood oil were exand., showing the following consts. resp.; I no. 149.6, 154.2; sapon. no. 196.1, 191.3; acid no. 5.4, 3.7. The fresh oil yielded 77.1% pure a -eleostearic acid. Isomerization of the a -eleostearic acid by Br., the freshly prepared CO_-dried - a eleostearic was brominated in ether at -10° and after "removal of the solvent the straw-colored sirup was cryst. from petroleum ether in the ice chest. The pptd. solid bromide m. $113-4^{\circ}$, the liquid bromide was a viscous light colored sirup, which remained unchanged for 4 weeks. The solid bromide proved to be a tetrabromide which on debromination by Rollett's method with Zn, MeOH and acid furnished a liquid acid, which could either be a-linolic acid or an isomer of a -eleostearic acid. By the same method of debromination the liquid bromide yielded the solid β -eleostearic acid, m. 72°. These results are discussed but no final conclusions are drawn. The same procedure of bromination and debromination was applied to the β -acid, yielding as final products solid B-eleostcaric acid both from the solid and the liquid bromide. No final conclusions are reached. Turbidity on drying and wrinkling of the film are probably not due to the formation of β-eleostearic glyceride; want of full information prevents a complete explanation." From C. A.

Eldred, F. H., and Lathrap, C. A.

A STUDY OF CRIENTAL CHINA WOOD (TUNG) OIL WITH RESPECT TO ITS ALPHA- AND BETA-FORMS. Am. Oil Chemists' Soc., Abstracts of Fall Meeting (24th) (Sept., 1950).

"This paper shows the results of analysis to determine the aand &-eleostearic acid content of a number of commercial shipments of China Vood Oil (Tung Oil) from China. Discussed also is the behavior of these oils when maintained at reduced temperatures, the proportions of the α - and β -forms in clear oil and in the solidified portion. An attempt is made to predict the lowest temperature at which an oil containing any given proportion of β -eleostearic acid will remain clear. The effect of the addition of β -eleostearic acid to the above oils, solution by warning, and subsequent chilling was also studied to obtain equilibrium data with wide ranges of variation of α - and β -acids. The rate of increase of β -eleostearic in commercial tung oils when these oils are stored at elevated temperatures is also studied. A comparison of total α - and β -forms in oils produced in China and in this country is shown." From Program, 24th Fall Meeting, Am. Oil Chemists' Soc., Sept. 1950.

Fahrion, W.

WOOD OIL AND LINSEED OIL.

Farben-Ztg. 17, 2530-2, 2583-4, 2635-6, 2689-91 (1912); Seifensieder Ztg. 39, 1089-90 (1912) (abstract); C. A. 7, 269, 710 (1913). "Large numbers of expts. and analyses lead F. to conclude: Wood oil contains about 10% oleic acid (not 25% (cf. Cloez, Compt. rend., 1875, 81, etc.)) and 2-3% satd. fatty acids. It can gelatinize (a) because of mol. rearrangement, through the action of light which takes place at ordinary temps., giving a cryst. compd. (m. about 32°), sol. in ordinary solvents or (b) by polymerization, which requires a temp. of 150° or over and yields insol. amorphous substances without definite m.p. Both forms of gelatinization also take place in absence of air at room temp. Wood oil "sets" more rapidly than linseed, although complete drying is slower. Drying action always begins on the surface as in the case of all other drying oils. Chemistry of the drying process is entirely analogous to that of linseed oil. Acids derived from oil gelatinized through polymerization are sol. in petroleum ether; those found in auto-oxidation process are insol. When drying oils are absorbed by purified cotton exposed to air, even the inner portions of oil take up 0 and the drying process may be followed quantitatively as in the case of oil films on glass slides. The dried oil films may also be examd. analytically (sapon. no., etc.) since the cotton is unaffected by alc. alkali. In the production of papier mache', by "baking" auto-oxidation, not polymerization, causes solidification of oil." From C. A.

Fokin, S.

THE ROLE OF METAL HYDRIDES IN REDUCTION PROCESSES AND NEWER DATA FOR CLARIFICATION OF THE QUESTION OF THE COMPOSITION OF MANY FATS AND MARINE OILS.

J. Russ. Phys. Chem. Soc. <u>38</u>, 419-46 (1906) *; Z. Electrochem. <u>12</u>, 759 (1906) *; Chem. Zentr. <u>1906</u>, III, 758-9.

Tung oil gives a third isomer of stearic acid, m.p.47° C., which, erroncously, was called eleomargaric acid as it was supposed to contain only 17 **C** atoms. Kametaka stated it contains 18 C atoms. F. confirmed this by reducing tung oil acids to a product from which he obtained a fraction which gelatinized at 68.5-67.8°, melted at 70.9-71.9 and had a mol. wt. of 280.1 (evidently stearic acid). The unsaturated acid absorbed bromine to form a tetrabromide, hence it must be analogous to linoleic acid.

Francois, M. Th.

GELATION OF THE ALEURITES OILS, CALLED CHINA WOOD OILS, BY THE HALOGEN SALTS OF ANTIMONY.

Compt. rend. 198, 1046-8 (1934).

The gelation of the China wood oils by heat or by the action of chemicals (iodine, nitrous acid, hypochlorous acid, ferric chloride, chlorides of sulfur, of aluminum or of zinc, etc.) requires a length of time that is sometimes rather long (several hours or even a whole night). They sometimes need rather delicate operating conditions. The method, described here, which uses a 10% solution of SbCl3 in chloroform offers the advantages of being rapid, requiring only common equipment and of presenting no difficulties of manipulation.

Francois, M. Th.

THE JELLIFICATION OF OILS FROM ALEURITES, SO-CALLED CHINESE WOOD OILS, BY HALOGEN SALTS OF ANTOMONY.

Bull. sci pharmacol. <u>41</u>, 269-71 (1934); C. A. <u>28</u>, 4921 (1934). "The jellification of China wood oils by heat or chem. agents like I, HNO₂, HCl, FeCl₃, S₂Cl₂, AlCl₃ or ZnCl₂ requires the observation of very accurate conditions and variable time. A 10% soln of SbCl₃ produces an instantaneous jellification. A comparison between a sample of pure oil and an unknown oil permits the detection of adulterants in the latter by the delayed time of solidification." From C. A.

Gardner, H. A.

LIME FOR THE VARNISH INDUSTRY.

Paint Mfrs. Assoc. U. S. Circ. 113, 1-20 pp. (Jan. 1921). Several tests for lime are described including one which measures the reactivity of the lime with tung oil (formation of calcium tungate) and which is carried out as follows: In a 100 cc beaker, place 50 grams of raw tung oil. Stir in 1 gram of lime. A cloudy mass will result. Apply heat. High quality hydrated lime will usually start to react at about 80° C., small bubbles rising to the surface. As heating is continued, large flakes of lime tungate will form and rise to the surface to form a thick white scum. On cooling, this scum, when freed from air, will drop to the bottom of the beaker. These tung oil soaps of lime are quite insoluble in the oil. A poor grade of lime will fail to react.

Gardner, H. A.

A BRIEF STUDY OF THE PHYSIOLOGICAL EFFECTS OF TUNG OIL PRODUCTS ON RABBITS AND DOGS WITH A NOTE ON PERCENTAGES OF ACCELERATORS FOR PRODUCTION OF BET.-ELEOSTEARIN FROM TUNG OIL. Paint Mfrs. Assoc. U. S. Circ. 270, 13-6 (1926); C. A. 20, 2370 (1926).

"G. concludes that (1) raw tung oil and β -eleostearin appear to have only mild carthartic effects in relatively large doses. (2) No irritating effect on the intestinal mucosa is produced. In the note on β -eleostearin the yields are given for its formation in tung oil in the presence of varying amts. of S. 0.02% S added to the oil and exposed to sunlight yielded no polymer in 48 hrs., and 23.5% after 1 week. One % S yielded 26% polymer in 48 hrs., and 23.5% after 1 week. Five % S yielded 28% in 48 hrs., 49% in 1 week." From C. A. Hannewijk, J., Otor, K., Vlodrop, C., van, and Waterman, H. I. THE ADDITION OF PHENOL TO FATTY OILS IN THE PRESENCE OF SULFUR DIOXIDE AND SULFURIC ACID.

Vcrfkroniek 13, 162-4 (1940); Paint Ind. Mag. <u>56</u>, 48 (1941); C. A. <u>35</u>, 6136 (1941).

"Considerable heat is evolved when tung oil (I) reacts with PhOH (II) in presence of HCl, SO₂ or H₂SO, to form viscous products. The increase in viscosity is believed due to addn. of I across one of the conjugated double bonds. Distd. Et eleostearate (III) (sp. gr. 0.891; n_{20} 1.4935) was made to react with 50% II and 12.6% SO₂ at room temp. for 16 hrs., the SO₂ was then expelled with N₂ and unreacted II driven off under high vacuum at 100°, leaving a residue (d. 0.9463; n^{D} 1.5020) which contained 14% combined II. A similar product obtained by reaction of III with II in presence of H₂SO₄ could be distd. under high vacuum. The reaction products of II with either I or III have a diene no. of 0 and do not split off II on heating to 100° or on refluxing with concd. HCl or 0.5 N

alc. KOH. The reaction products probably contain a phenolic OH group." From C. A.

Hansley, V. L.

SODIUM REDUCTION OF FATTY ACID ESTERS.

Ind. Eng. Chem. 39, 55-62 (1947); C. A. 41, 1202-3 (1947).
"The Na reduction of tung oil (glyceride of eleostearic acid)
yields an alcohol containing only 2 double bonds, presumably
an isomer of linoleyl alcohol. Detailed procedures and a
bibliography are given." From C. A.

Hilditch, T. P., and Smith, C. J.

CONDENSATION OF 2,6-DILETHYLOL-P-CRESOL WITH ESTERS OF HIGHER FATTY ACIDS.

J. Soc. Chem. Ind. 54, 111-15T (1935); C. A. 29, 4611 (1935). "H. and S. studied the condensation of 2,6-dimethylol-p-cresol (I) with Me palmitate, Me oleate, Me linoleate, Me linolenate, Me esters of tung oil, and with raw linseed oil, boiled linseed oil, raw tung oil and paraffin wax. Analysis of the unchanged esters, extd. with petr, ether, indicated that esters of satd. and mono-ethylenic acids may undergo some displacement to form the esters of I, but that no other condensation with I takes place; esters of di- and poly-ethylenic acids condense with I at the unsatd. centers to form resins. The condensation with tung oil proceeded farthest; boiled linseed oil reacted more readily than did the raw oil. Triglyceride mols. contg. 3 polyethylenic acids condensed with I more readily than did glycerides - contg. one satd. or oleic radical. Failure of paraffin wax to react further indicates that aliphatic methylene hydrogens are not involved in condensations of oils with I." From C. A.

Holde, D., Bleyberg, W., and Aziz, M. A.

HALOGEN ELIMINATION FROM H.LOGENATED ELEOSTEARIC ACID. IDENTIFICATION OF PHTHALIC ACID BY THE FLUORESCEIN REACTION. Z. angew. Chem. <u>42</u>, 283-4 (1929)*; C. A. 23, 3215 (1929)

"Unsatd. acids which have been treated with excess IBr in glacial AcOH (Hanus reagent) and the excess titrated with $Na_2S_2O_3$, spontaneously liberate the added halogen (cf. Holde, C. A. 23, 2049 and Kaufmann and Lutenberg, C. A. 23, 3360. Expts. were made to det. if the loss of halogen in the case of dibromo -eleostearic acid (I) gives an aromatic acid which can be exidized with CrO₃ to phthalic acid (II) as follows:

$$\overset{\text{Me}(CH_2)_3\text{CH:CHCH:CHCH:CH(CH_2)_7}}{\longrightarrow} \overset{\text{Me}(CH_2)_3\text{CHBrCH:CHCH:-}}{\longrightarrow} \overset{\text{Me}(CH_2)_3\text{CHBrCH:CHCH:-}}{\xrightarrow} \underset{\text{CHCHBr(CH_2)_7}}{\longrightarrow} \overset{\text{CHCHCH:-}}{\xrightarrow} \underset{\text{CHCHBr(CH_2)_7}}{\longrightarrow} \overset{\text{Me}(CH_2)_3\text{CHBrCH:CHCH:-}}{\xrightarrow} \underset{\text{CHCHBr(CH_2)_7}}{\longrightarrow} \overset{\text{CHCHCH:-}}{\xrightarrow} \underset{\text{CHCHBr(CH_2)_7}}{\longrightarrow} \overset{\text{CHCHCH:-}}{\xrightarrow} \underset{\text{CHCHBr(CH_2)_7}}{\longrightarrow} \overset{\text{CHCHCH:-}}{\xrightarrow} \underset{\text{CHCHBr(CH_2)_7}}{\longrightarrow} \overset{\text{CHCHCH:-}}{\longrightarrow} \overset{\text{CHCHCH:-}}{\xrightarrow} \underset{\text{CHCHBr(CH_2)_7}}{\longrightarrow} \overset{\text{CHCHCH:-}}{\longrightarrow} \overset{\text{CHCHCH:-}}{\longrightarrow} \overset{\text{CHCHCH:-}}{\longrightarrow} \overset{\text{CHCHCH:-}}{\longrightarrow} \overset{\text{CHCHCH:-}}{\longrightarrow} \overset{\text{CHCHCH:-}}{\longrightarrow} \overset{\text{CHCHCH:-}}{\longrightarrow} \overset{\text{CHCHCHCH:-}}{\longrightarrow} \overset{\text{CHCHCH:-}}{\longrightarrow} \overset{\text{CHCHCHCH:-}}{\longrightarrow} \overset{\text{CHCHCHCH:-}}{\longrightarrow} \overset{\text{CHCHCHCH:-}}{\longrightarrow} \overset{\text{CHCHCHCH:-}$$

$$(alc. KOH, 130^{\circ}) \xrightarrow{o-Me(CH_2)_3C_6H_4(CH_2)_7CO_2H} (II)$$

The oxidation product when heated for 3 min. with resorcinol (III) and 1 drop H_2SO_4 at 160° gave a fluorescent soln. in dil. alkali but this was not due to the presence of II since many other compds., viz., aldehydes, ketones, chlorides, mono- and dibasic acids, and esters give condensation products with III which yield fluorescent alk. solns. (acetfluorescein, succinylfluorescein, etc.). When making a test for II it is essential that no H_2SO_4 be added and that the condensation with III be brought about at 205-10° for 3 mins. Whether the loss of halogen from I gives oxygenated or polymerized products was not detd. and further investigations are under way to det. the course of the reaction." From C. A.

Hollander, A.

BLOWN LINSEED OIL, SULFO-LINSEED OIL AND SULFO-TUNG OIL. Farbon-Ztg. 36, 118-20 (1930); C. A. 25, 221 (1931). "The superior waterproofness of films of sulfo-oils and blown oils is ascribed to a twofold gel structure which is present in the liquid oil. In addn. to the structure due to ordinary at. valence forces there is superimposed one due to mol. valence forces. S in particular is bound to the oil mols. by the latter. I and acid nos. obtained during aging of films of blown and sulfooils are given in support of the above theory." From C. A.

Hopkins, F. W.

A PHENOMENON TO BE CONSIDERED IN THE STORAGE OF CHINA WOOD OIL. Am. Paint Varnish Mfrs. Assoc. Circ. 74. 297, 28-31 (1927); C. A. 21, 658 (1927).

"A description of the formation of the solid β -eleostearin modification; theoretical explanations are offered." From C. A.

Ishio, M.

BROMINE DERIVATIVES OF ELEOSTEARIC ACID.

J. Pharm. Soc. (Japan) No. 501, 789-96 (1923); C. A. 18, 815 (1924). "a-eleostearic acid (I), prepd. by sapon. of paulownia oil m. 48°. An attempt to prep. the tetra-Br deriv. from I in glacial AcOH was not successful (cf. Nicolet, C. A. 15, 1723), neither could a di-Br deriv. be prepd from the Et₂O soln. at 25° as N. recommends. By varying the temp. and solvents, I. obtained different Br derivs. When 150 g. I in 5 l. Et 0 were treated with Br at -15° 73 g. of a di-Br deriv. (II), C₁₈H₃₂Br₂O₂, m. 91°, were obtained. If II in CHCl3 is treated again with Br at -15° the tetra-Br-deriv. C₁₈H₃₂Br₄O₂ (III), m. 115°, is obtained. An identical tetra-Br deriv. can also be prepd. by directly brominating I in CHCl₃ (35% yield). When II is treated with cold KOH, unsatd. fatty acids (one of which has the compn. $C_{18}H_{32}O_2$), are obtained which are converted into stearic acid by catalytic hydrogenation with Pt. black. A similar treatment of III gives another di-Br deriv., C₁₈^H Br O, m. 40-0.5°, which has entirely different properties from II." From C. A.

Kass, J. P., and Burr, G. O.

PSEUDO-ELAEOSTEARIC ACID.

J. Am. Chem. Soc. 61, 3292-3294 (1939); Brit. Chem. Abstracts

1940, A, II, 64. ^{II} W Elaeostearic acid, m.p. 77-79° (uncorr.) (Me ester, m.p. 41°), is propared by heating linseed oil fatty acids with KOH, best in BuOH or (CH2.OH). It is hydrogenated (PtO2; AcOH) at 3 atm. to stearic acid and with KMnO_4 in COMe_2 gives sebacic acid, $\text{H}_2\text{C}_2\text{O}_4$, and PrCO_2H . It is thus Δ^{λ} - octadecatrienoic acid. It readily forms a tetrabromide, m.p. 104-104.5°, but the hexabromide, m.p. 152.5° is smoothly obtained only in ultra-violet light. With maleic anhydride in N2 at 145°, it gives a mixed adduct, sinters at 75°, m.p. 77°, clcar at 82°, and is thus the trans-trans-or trans-cis-trans- compound. The absorption spectrum accords with the triple conjugations." From Brit. Chem. Abstracts.

Kaufmann, H. P.

FATS. XIII. PARTIAL ADDITION OF HALOGEN TO POLYUNSATURATED FATTY ACIDS. GLYCERYL BETA-ELAEOSTEARATE AND WOOD (TUNG) OIL. Ber. 62, 392-401 (1929); Brit. Chem. Abstracts 1929, B, 291.

"Glyceryl β -elaeostearate when treated with a 100% excess of bromine in carbon tetrachloride in the absence of light absorbs 2 mols. of halogen in the interval 3-8 hrs., after which addition commences at the third double linking. Determination of the corresponding iodine value in tung oil is effected by mixing 0.1-0.15 g. of the sample in 10 cc of pure carbon tetrachloride with 30-40 cc of 0.1 N-bromine in the same solvent, preservation of the mixture in the dark for 4-5 hrs. addition of aqueous potassium iodide, and titration of the liberated iodine. Subsequent addition of potassium iodate to the solution causes only very slight liberation of iodine, so that substitution has not occurred to an appreciable extent. For the determination of a single unsaturated linking, glyceryl β -elaeostearate or tung oil (0.1-0.12 g.) is dissolved in a mixture of equal volumes of chloroform and carbon tetrachloride (distilled over phosphoric oxide). A solution of (20 cc) of bromine and iodine is added prepared by addition of the requisite weight of iodine to a 0.1 M-solution of bromine in methyl alcohol containing sodium bromide. After 3-4 hours the mixture is treated with 5% aqueous potassium iodide and the liberated iodine is titrated. The "partial iodide value" thus determined coincides with or differs by 1-2 units from the thiocyanogen value." From Brit. Chem. Abstracts.

Kaufmann, H. P.

ISOLATION OF ADDITION PRODUCTS OF THIOCYANATE IN UNSATURATED ACIDS. Chem. Umschau Fette, Oele, Wachse. u. Harze <u>37</u>, 113-7 (1930); C. A. 24, 4177 (1930).

"Details are given for the preparation of dithiocyanostearic acid from oleic, elaidic and petroselenic acids, 13,14-dithiocyanobehenic acid from erucic acid and hexathiocyano- β -eleostearin from β -eleostearin." From C. A.

Kawai, S.

AN ATTINPT TO PREPARE HIGHER UNSATURATED ALCOHOLS FROM SOME DRYING OILS.

J. Chem. Soc. Japan <u>49</u>, 227-34 (1928)*; C. A. <u>24</u>, 63 (1930). "K. reduced tung oil, linseed oil and sardine oil with AmOH, Na and PhMe and obtained the mixt. of unsatd. alc. and cetyl alc.

This reduction process will apply to the detection of A ²-hypogenic acid and satd. fatty acid in these oils. K. obtained a large amt. of cetyl alc. on the reduction of sardine oil, and he therefore suggested that there was A.²-hipogenic acid in it beside palmitic acid. On the reduction of the fatty acid of sardine oil he confirmed that there is present an unsatd. C₂₀ fatty acid. On the reduction of tung oil he obtained a large quantity of unsatd. aliphatic alc., $C_{18}H_{3\mu}O$, $F_{-\mu}$ and he named this alc. isodihydroeleostearin alc. He also obtained $C_{18}H_{32}O_2$, $F_{-\mu}$ on the reduction of a-eleostearic acid, by the same method with good yield and named it isodihydroeleostearic acid." From C. A.

Krumbhaar, Wm.

ON VELOCITY REACTIONS IN FAT CHEMISTRY. I.

Chem. Rev. Fett-u. Harz Ind. 20 (10), 232-237 (1913).

The velocity of saponification was studied by the cold method of Henriques on linseed oil, bodied linseed oil, wood oil and mixtures of linseed and wood oils. Rate differences were slight and became apparent only after long reaction times. Krumbhaar, Wm.

ON VELOCITY REACTIONS IN FAT CHEMISTRY. II.

Chem. Rev. Fett u. Harz-Ind. 20 (11), 260-3 (1913).

Iodine absorption measurements were made on several oils, fats and resins by the Hubl-Waller method. Two samples of wood oil which were tested using a copper chloride catalyst gave iodine numbers of 154 and 148. Wood oil differs from linseed oil in that it adds some iodine very rapidly and the remainder very slowly.

Krumbhaar, Wm.

THE REACTIVITY OF STRAIGHT PHENOLIC VARNISH RESINS. J. Oil & Colour Chemists' Assoc. <u>19</u>, 363-8 (1936); C. A. <u>31</u>, 5603 (1937).

"K. differentiates between "dialcohol" resin (I) made by condensing PhOH with CH_O using alk. catalysts and "complex phenol" resins (II) made by condensing PhCH with compds. of methylene structure (such as Me₂^{OO} or unsatd. hydrocarbons) in presence of an acid catalyst. In the varnish kettle, the alc. groups of type I resin condense with themselves causing foaming and also link up other mols. by reacting with their reactive H, while the unsat. bonds enter into the reaction to a slight though definite degree. Resistance to water and the weather is thereby improved without drying being impaired. Type II resins react with the unsatd. centers present, e. g., in abietic acid or linseed oil, while little if any self-condensation goes on, foaming is not observed and there is little if any linking action as with I. With II, durability is improved, but drying tendency is somewhat reduced. Tung oil reacts with both I and II by the diene synthesis to yield products of great tech. value. In all cases, chem. reaction is essential to producing durable varnish, as simple phys. dispersion of resins in oil fails to yield materials having satisfactory resistance." From C. A.

Kurz, H.

THE CATALYTIC ALCOHOLYSIS OF FATTY OILS WITH ALCOHOLIC POTASH. Fette u. Seifen <u>44</u>, 144-5 (1937); C. A. <u>31</u>, 8967 (1937). "Data on the alcoholysis of olive oil, sesame oil, linseed oil, linseed-oil stand oil, tung oil and tung-oil stand oil are tabulated. The glyceride splitting must be rather far advanced before large proportions of glycerol are liberated. This is due to the intermediate formation of mono- and di-glycerides as shown by Acetyl nos. and sapon. nos. Rate of glyceride splitting increased with increasing water content of the alc. and also with increasing KOH concn., even when the ratio of KOH to fat was kept const. The slower the glyceride splitting. Substantial differences in the rate of alcoholysis of the different fat acids in stand oils were not observed." From C. A.

Lippert, W.

LINSEED OIL, VARNISH OILS AND OIL PAINTS Z. angew. Chem. <u>1897</u>, . 779-82. Various oils were mixed with ZnO. Chinese wood oil gave a cheese-like product.

Loon, J. van

THE BROWLIDES OF THE ELEOSTEARIC ACIDS. I. THE HEXABROWLIDES. Rec. trav. chim. 50, 32-6 (1931); C. A. 25, 2689 (1931). "Recent researches have shown the eleostearic acids have the formula Me(CH₂)₃CH:CHCH:CHCH:CH(CH₂)₇CO₂H(Eibner and Rossmann, C. A. 22, 4839; Boeseken, C. A. 23, 5160; van Loon, Diss. Delft, 1929, 62; C. A. 24, 4178). The formation of hexahalogen compds., however, does not take place easily and Kaufmann was the first to show the presence of 3 double bonds (C. A. 20, 2989) titrimetrically although he did not isolate any hexa-Br compd. In order to prep. these compds. β -eleostearic acid was brominated in CCl_L with the theoretical amt. of Br under the influence of Uviol light after it had been shown that this light does not provoke any particular intramol. change. After evapa. of the solvent and recrysta. of the residue from petroleum ether to which a small amt, of ether had been added, 0.5 g. of the hexabromide, m. 157°, was obtained from 7 g. of the acid. On debromination with Zn and alc. HCL the hexabromide gave & -eleostearic acid in quant. yield; the same acid was again obtained on debrominating the only mixt. of hexabromides which results after sepn. of the cryst. compd. The same cryst. hexabromide was also obtained from a-eleostearic acid, which is easily converted into the β -form by traces of halogen; therefore most probably the hexabromides are formed in both cases from the same mixt. of tetrabromides which are formed as the primary reaction products, tetrabromination taking place instantaneously and further bromination only very slowly. The solid tetrabromide, m. 114°, on bromination gives the same hexabromide, m. 157°, the yield being only 10 g. from 100 g. of the tetrabromide; in this case again the oily hexabromides on debromination gave B-eleostearic acid." From C. A.

Loon, J. van

BROMIDES OF ELAEOSTEARIC ACID. II. TETRABROMIDE. Rec. trav. chim., <u>50</u>, 638-644 (1931); Brit. Chem. Abstracts 1931, A, 822.

"Elaeostearic acid tetrabromide, m. p. 114.8°, interacts only very slowly with Wijs' solution, 6-8 weeks' contact being needed for the theoretical absorption of Cl; no absorption of Br occurs from Kaufmann's solution. In view of the comparative ease of determination of the unsaturation of elaeostearic acid by both these methods it is concluded that the cryst. tetrabromide is a product of rearrangement of the original tetrabromide formed in solution." From Brit, Chem, Abstracts, Marcusson, J.

SOME REACTIONS OF TUNG OIL AND ELEOSTEARIC ACID.

Farben-Ztg. 37, 1354 (1932); C. A. 26, 4725 (1932).

"Tung oil treated with HNO3 or H2SO4 polymerizes with the formation of a solid product; with the latter a S-contg. compd. is also formed. For quant. purposes the HNO3 reaction is preferred. Ten cc. of oil in 20 cc. C6H is shaken with 1 cc HNO3 in a separatory funnel. After a short period the reaction is stopped by dilg. with H2O. Ten % tung oil can be detected. The stages in the drying of tung oil are the formation of β glycerides, polymerization and finally oxidation. Light, peroxides in the air, and other agents, e.g., I, are able to produce the first two steps. The insol. form of the β -glycerides is due to polymerization." From C. A.

Merz, 0.

TETRABROMIDE OF ELEOSTEARIC ACID.

Farben-Ztg. 33, 2423-4 (1928); C. A. 23, 1873-4 (1929). "A review of published work on the bromination of the eleostearic acids. Expts. on the m. p. of mixts. of the tetrabromides of a - and β -eleostearic acids support the view of Rollett (C. A. 5, 1741) that isomerization from the α - to the β form occurs on bromination, the β -form remaining unaffected." From C. A.

Miller, E. S., Brown, W. R., and Burr, G. O.

ABSORPTION SPECTRA OF LIPIDES AND THEIR APPLICATION TO METABOLIC STUDIES · Oil & Soap 15, 62-5 (1938); C. A. 32, 3439 (1938).

"Absorption curves are given for some purified fat acids, com. oils and tissue lipides. There is a specific absorption band for fat acids at about 2300 A. Many lipides have absorption coeffs. far too high to be accounted for by the well-recognized fat acids. It is shown that this is not related to degree of unsatn. but is best accounted for by conjugation of double bonds. Hence absorption spectra serve as one of the best quant. measures of conjugation in its various forms. In metabolism the rat attacks only one of the bonds in eleostearic acid at a time leaving the other 2 for a sufficient period to be measured spectroscopically." From C. A.

Morrell, R. S., and Marks, S.

ONID TION PRODUCTS OF DRYING OILS. I. BETA-ELEOSTEARIN FROM TUNG OIL. J. Soc. Chem. Ind. 50, 27-36T (1931); C. A. 25, 1689 (1931).

"In the oxidation of the β -eleostearic glyceride the first product is a diperoxide, followed by a change to a monoperoxide, $(CH_3(CH_2)_3CH, CH, CH: CHC(OH: C(OH)(CH_2)_7 -)_0$



COO)₃C₃H₅. On methylation, Me esters, sol. and insol. in light

petroleum, are formed. The max. number of methoxyl groupings which can be introduced is two. Attempts to methylate Me ricineolate were unsuccessful and resulted in the production of a methyl ester of an acid isomeric with linoleic acid. The Me esters are oxidized by KMnO_4 to valeric acid and an intermediate C_{13} or C_1 acid. Reduction by H_2 with Pd causes addition of 2 or 4 atoms of H. Treatment of the Me esters with HI or HBr causes reduction of the peroxide group and withdrawal of the methoxyl groups to form $\text{CH}_3-(\text{CH}_2)_3\text{CH-CHCH:CHCHCH(CH}_2)_7\text{CO}_2\text{H}}$. The evidence in favor of pos. and

neg. polarity of the peroxide groups has been strengthened. The yellowing of drying films is due to rancidity, caused by disruption of the remote peroxide and the action of strong bases on the near peroxide to form colored salts. The inert character of the central double linking is very marked. There is a strong associating power of both peroxide groups. The peroxides are very stable in acid media. Polymerization of the oxidized esters is accompanied by a rise in refractive index. The loss in wt. of linoxyn films is connected with degradation beginning at the remote peroxide grouping. A scheme of orientation on the lines of Staudinger's representation of polymerides is suggested." From C. A.

Morrell, R. S., Marks, S., and Samuels, H. THE DOUBLY CONJUGATED SYSTEM IN THE GLYCERIDES OF ALPHA- AND BETA-ELEOSTERATIC ACIDS. J. Soc. Chem. Ind. 52, 130-2T(1933); C. A. 27, 3349 (1933). "The prepn. and properties of the maleic anhydride compds. of a- and β- eleostearin from tung oil are described, and it is shown that only the β-eleostearin gives thermo-hardening

Mundy, C. W. A.

MONOGLYCERIDES OF THE DEVING OILS.

films suitable for varnishes." From C. A.

Chim. peintures 2, 93-7 (1939).

Monoglycerides can be prepared by reacting fatty acids with glycerol, soaps with monochlorhydrin, or triglycerides with glycerol. By the last method monoglycerides have been prepared from linseed, perilla, soybean, castor, dehydrated castor and wood cils. The latter are chiefly of academic interest because their great reactivity is almost uncontrollable. Monoglycerides react with resins such as gun lac, Kauri and Copal Congo to form products useful in making lacquers. The reaction between gum lac and mono-glycerides is catalysed by the presence of small amounts of China wood oil. Nakamura, Mitsuo.

PEROXIDES OF FATTY OILS.

V. DECOMPOSITION REACTION OF SOYBEAN OIL PEROXIDES AT 130° AND THE INFLUENCE OF ANTI-OXYGENS, PROOXYGENS AND SOLID POWDERS THEREUPON. VI. FORMATION AND DECOMPOSITION OF FEROXIDES OF SOME FATTY OILS.

J. Soc. Chem. Ind., Japan <u>40</u>, Suppl. binding 229-30, 230-2. (1937); C. A. <u>31</u>, 7681 (1937).

"Old soybean oil contg. 0.2% of active 0 was used as a sample, various substances were added and the 10-g. sample was dipped in the 130° oil bath and held for 55 to 60 min. after the temp. reached 130°. Antioxygens, hydroquinone and a -naphthol and prooxygens, p-nitraniline, jara-jara and vanillin exert no influence on the decompn. of peroxides at 130°. Mn abietate and Pb linoleate accelerate the decompn. Japanese acid clay, Norit active C and kieselguhr accelerate the decompn., the effect decreasing in the order given. The optimum temps. of formation of peroxides of Japanese tung oil, linseed, tsubaki and castor oils were detd. as 95°, 105°, 125-40° and 155°, resp, the quantities of peroxides produced are least for castor oil and tung oil is next. The reason for the small amts, of peroxides in tung oil is due to the property of the glycerides of a-eleostearic acid; for the I no. of the oil blown for 90 min. was 137.8 while the I no. of the original oil was 143. In order to det. Why less peroxides are produced in the oils of higher unsath. the relation between the quantities of peroxides and the apparent 0 absorption was investigated by exposing the oils to ultraviolet rays at 40°. It was found that the velocities of formation of peroxides in tung and castor oils are smaller than those in linseed and tsubaki oils. The results show that the process involved in the oxidation of conjugated double bonds is somewhat different from that of other unsatd. bonds. The decompn. temps. of peroxides of tung, linseed, tsubaki and castor oils were detd. after the oils were irradiated by ultraviolet light at 30°. The peroxides of tsubaki oil are the most stable and begin to decomp. at 130°. Castor and linseed come next and begin to decomp. at 110° and 80° resp. Those of tung oil are most unstable and start to decomp. at 40°. The difficulties of forming peroxides in tung and castor oils at blowing temps. above the decompn. temps. of the peroxides of these oils may partly be attributable to the thermal decompn. of the peroxides once formed into the stable oxide form. But since these peroxides are stable at low temps. in the presence of ultraviolet rays, the smallness of the amts. of the peroxides of these oils produced under irradiation at 40° cannot be ascribed so much to the instability of these peroxides as to the fact that the greater part of the conjugated double bonds are oxidized directly to oxide forms without making peroxides." From C. A.

5 2 . 5

Nasini, A. G., and Ghersa, P.

OXIDATION REACTIONS OF DRYING OILS IN UNIMOLECULAR LAYERS. Atti X° congr. intern. chim. <u>4</u>, 236-49 (1939)*; C. A. <u>34</u>, 3932 (1940).

"The oxidation of unimol. layers of linseed oil (I), and China wood oil (II) and their components by air, KMnO₁, and O₃ or its equiv., irradiation by a Hg-vapor lamp, is represented by force-area curves. Autoxidation of I is slow and produces slight expansion as compared with the other oxidizing agents. Under the influence of O₃, formation of hydroxystearic acids is indicated. Triolein behaves similarly to I. Oleic acid expands when treated with KMnO₄ and contracts when irradiated. Linoleic and linolenic acids contract in contact with KMnO₄ and irradiation. II contracts under autoxidation to a gelatinous mass and reacts toward the other oxidizing agents like I. β -Eleostearic acid, β -eleostearin (III) and the compd. (IV) of III with maleic anhydride (C. A. 26, 5545) expand under the action of KMnO₄ and irradiation. The effect of irradiation on III and IV is modified by pressure." From C. A.

Normann, W.

CHINESE WOOD OIL (TUNG OIL).

Chem. - Ztg. <u>31</u>, 188 (1907); J. Soc. Chem. Ind. <u>26</u>, 262 (1907). "Chinese wood oil remained practically unaffected by exposure to light for one week in a sealed glass tube. On saponifying the cil, the clear scap solution remains unaltered if kept in the dark, but on exposure to light, fine crystals gradually separate. The free fatty acids are also sensitive to light, and become polymerised. On heating the oil to <u>300°-520°</u> C. in a sealed tube, polymerisation proceeds further, and is accompanied by slight decomposition. Oil which are become solid by exposure to light undergoes further change on heating, but oil already polymerised by heat is not affected by exposure to light." From J. Soc. Chem. Ind.

Oda, R., and Wada, S.

THE ACTION OF AMMONIA UNDER HIGH PRESSURE UPON ORGANIC COMPOUNDS. I. AMMONOLYSIS OF FATTY OILS.

J. Soc. Chem. Ind., Japan <u>37</u>, Suppl. binding 295-6 (1934); C. A. 28, 6005-6 (1934).

"The expts. were carried out in a shaking autoclave at 150°. Olive oil, coconut oil, castor oil, fish oil, spermacabl, wood cil and linseed oil were treated with 100 cc. of liquid NH₂ per 100 g. of substance. The heating periods were 0.5 and 1 hr. for olive oil and 1 hr. for all others and the pressure was 80-100 atm. The I no., sapon. no. and N content (Kjeldanl) are reported for the treated products. The ammonolysis gave good yields of acid amides. All products were solids. The coconut oil product yielded 70-80% of distillate at 1 cm. Hg pressure, m. 100°, which had a N content of 6.3%." From C. A.

Pontius, A. W.

CHINESE WOOD OIL.

Consular and Trade Reports No. 3233, 12-13 (July 22, 1908) * Dept. of Commerce and Labor, Washington, D. C.; Paint, Oil Drug Rev. p. 28, (July 29, 1908); Oil, Paint Drug Reptr. p. 22, (July 27, 1908).

A brief, general review with emphasis on the properties of the oil. Heating the oil (100 parts) with white manganese borate (3) at 270° C. until a scum rises and then adding benzine (700) gives, after a few days, a thick water-white liquid resembling gelatine.

Reutenauer, G.

TRANSESTERIFICATION OF CHINA WOOD OIL WITH COLZA OIL OR CURCAS OIL. Bull. mens. ITERG (Inst. tech. etudes et recherches corps gras) 1948, 8, 28-31*; C. A. 43, 1992 (1949).

"Investigation of the problem up to what extent colza oil (I) and curcas oil (II) can be added to China wood oil (III) to give an economical substitute for III. Simple blending of equal parts of III and I or III and II increases the drying time to approx. 6 days (III alone; 1 day). Transesterification of the same mixts. by heating them in CO2 atm. with 0.02% of Ca naphthalene at 200° for 6 to 10 hrs. reduces the drying time to resp., 1.5 and 2.5 days, but the adhesion of the film is bad. Heating to 230° leads to unobjectionable films but the drying time is slightly increased. Mixts. of I and II with previously standolized III dry faster than if raw III is used; transesterification is in that case uncapable of lowering further the drying time, and the hypothesis is advanced that standolization is accompanied by modifications of structure hindering transesterification. Expts. are tabulated showing the influence of different working conditions on drying power, viscosity, color, and acidity of various mixts." From C. A.

Scheiber, J.

THE CATALYTIC EFFECT OF OXYGEN ON TUNG OIL.

Farbe u, Lack 1929, 284-6; C. A. 23, 4087 (1929).

"When tung oil is treated with small quantities of O_2 , I_2 , etc., the β -glyceride is formed; with large amts. of the reagent a polymerized product is formed. E. G., radial crystal formations of the β -glyceride were formed in tung oil preserved between a microscope slide and a cover glass. If crystals of the β -glyceride be dissolved in warm tung oil they reappear as very min. crystals, but if a trace of the original crystals be undissolved, they recrystallize normally." From C. A. Singer, Rudolf, Jr.

THE REACTION BETWEEN OIL-REACTIVE ALKYLPHENOL RESINS AND DRYING OILS. II. INVESTIGATIONS ON LACQUER.

Kem. Maanedsblad 23, 49-61 (1942)*; Chem. Zentr. 1942, II, 717; C. A. 37, 5876-7 (1943).

"After a review of the contradictory work and reactions taking place on cooking oil-reactive phenol resins with drying oils, S. finds that the conjugated double bonds of China wood oil, detd. by the aid of the diene no., and the double bonds of linseed oil, detd. by the I no., are more strongly consumed on cooking than with pure oil. Differences are found with different phenol resins. It is shown by tests that the reactivity can be attributed neither to free alkylphenols in the resin nor to CH₂O split off. The theory is advanced that the methylquinone, formed during the hardening of the phenol resin, as a philodiene component, undergoes reaction with the double bonds of the oil." From C. A.

Sorensen, S. O.

DRYING-OIL RESEARCH.

Official Digest Federation Paint & Varnish Production Clubs No. 236, 283-8 (1944); Am. Paint J. 28, (38), 51, 54, 56, 68, (1944); C. A. <u>38</u>, 4142 (1944).

"Lack of fundamental knowledge of oil chemistry and the unanswerable competition of china wood oil are responsible for slow development in drying oil. The accomplishments of the drying-oil industry to date and tasks to be undertaken in the immediate future are detailed." From C. A.

Steger, A., Loon, J. van, and Vlimmeren, P. J. van.

STUDIES ON TUNG AND OITICICA OILS.

Fette u. Scifen <u>51</u>, 49-53 (1944); J. Am. Oil Chemists' Soc. <u>24</u>, 182 (1947); C. A. 41, 1472 (1947).

"Hydrogenation experiments were run on samples of tung oil and the Me esters of tung and oiticia fat acids. Observed changes in I number, diene number and other constants are discussed from the standpoint of reaction mechanism. Derivatives are reported for β -couepic (licanic) acid and γ -ketostearic acid from oiticica and Po-Yoak oils. The oximes melt at 60° and 85.1° respectively and the semicarbazones melt at 137-8° and 119°." From J. Am. Oil Chemists' Soc.

Tatimori, M.

POLYMERISATION OF TUNG OIL. II. GELATION OF TUNG OIL BY CATALYTIC ACTION OF IODINE. Bull. Chem. Soc. Japan 15, 1940, 315-321*; Brit. Chem. Abstracts 1941, B, II, 16; C. A. 35, 4616 (1941).

"The gelation time (t) of tung oil in various solvents in presence of I is related to the concns. by log t = a (oil) + b/(oil)(I), a and b being consts. The accelerating action of I is strongest in violet and weakest in brown solutions, with the exception of org. acids and PhNO₂. Generally the effectiveness of the I increases with increasing ε of the solvent." From Brit. Chem. Abstracts. Tatimori, M.

GELATION OF TUNG OIL XIV. EFFECT OF SOLVENTS ON GELATION TIME OF TUNG OIL WITH IODINE AS CATALYST.

J. Soc. Chem. Ind. Japan <u>44</u>, Suppl. Binding 7-8B (1941); Brit. Chem. Abstracts 1941, B,II, 309.

"Gelation time has been measured in presence of I in 37 solvents. In halogenated solvents I accelerates gelation, but in oxygenated solvents it has little or no effect." From Brit. Chem. Abstracts.

Wagner, Hans.

INFLUENCE OF PIGMENTS ON TUNG OIL.

Farben-Ztg. 35, 179-82 (1929); C. A. 24, 513 (1930).

"Pignents ground in tung oil influence to a greater or less degree the sepn. of β -eleostearin, the greatest effect being caused by certain ultramarines, ZnS and lithopone. The sepn. was inhibited in some cases, notably by wet ultramarine, CaCO₃ and ZnO. The sepn. was studied by spreading the pastes on microscope slides and observing the rate at which the field was filled with crystals. In most cases the effect is probably mech. but acceleration may be due to active sulfides and inhibition to basic substances, e.g., ZnO, CaCO₃, etc." From C. A.

Waterman, H. I., and Vlodrop, C. van.

THE HARDENING OF CHINA WOOD (TUNG) OIL. Chimie & industrie Special No., 902-8 (April, 1934); C. A. 28, 5999 (1934).

"In the hardening of tung oil, there is no appreciable increase in the satd. acid content at the start of hydrogenation when the latter is carried out at relatively high temp. (180°) and by Norman's or Wilbuschewitsch's methods; the I no. may fall by 100 units while the satd. acid content increases only 3%. At lower temps (50-60°) and under very high pressure the satd. acid content increases right at the start of the operation. In this respect, the hardening of tung oil is quite similar to that of other vegetable and animal oils examd. to date by Waterman, et al. The sp. refraction of the products obtained by hydrogenation at low temp. is always lower than that of products showing the same degree of unsatn. but obtained by hydrogenation at high temp. This might indicate that the system of conjugated double bonds existing in eleostearic acid is better preserved by hydrogenation at low temp. Hydrogenation at 50-180° can be carried out without any polymerizations taking place. The curves representing n as a function of the H-I no., and d. as a function of the H-I no. are practically linear in certain regions." From C. A.

Waterman, H. I., and Vlodrop, C. van.

NATURE OF THE INTERMEDIATE PRODUCTS IN THE HYDROGENATION OF TUNG OIL UNDER VARIOUS CONDITIONS. Chem. Weekblad 31, 420-422 (1934)*; Brit. Chem. Abstracts 1934, B, 769.

"The relation between quantity of H_2 absorbed, I val., % of saturated acids, and in some cases n, dispersivity, and absorption spectrum during the hydrogenation of tung oil from <u>Aleurites</u> fordii, Et elaeostearate, β -elaeostearic acid and Et linoleate has been studied. The intermediate products vary with temp. pressure,

and catalyst, products with the same degree of hydrogenation not being necessarily identical. Complete hydrogenation of the tung oil products, without any polymerisation, can be effected at < 70° by using a special Pt-C catalyst. Pt and Pd catalysts can also be used; Ni is less efficient." From Brit. Cnem. Abstracts.

Wittka, F.

PRACTICAL TESTS ON PARTIAL HARDENING OF STRONGLY UNSATURATED OILS II.

Allgem. Oel-u. Fett-Ztg. 33, 515-18 (1936)*; C. A. 31, 1237 (1937). "Hydrogenation tests as carried out on linseed oil (C. A. 30, 7369) were repeated on perilla oil. There was no sharp increase in formation of isooleic acid with increase in temp. as was found with linseed oil at temps. between 70° and 90°. Perilla oil hardened 60 min. at 60° had an I no. 140.3 and that hardened for a like period of time at 70° had an I no. 120.5. Their resp. fat acid compns. were: solid satd. acids 9.0, 10.9; solid unsatd. acids 9.0, 21.5; oleic acid 11.0, 14.0; linoleic acid 66.0, 49.5; and linolenic acid 5.0, ---. The results show that when hydrogenating perilla oil the formation of solid unsatd. acids occurs even at very low temps. while with linseed oil only small amts. are formed at the low temps. Further research is recommended to explain this phenomenon. Chinese wood oil was investigated in like manner. The high solidification point of the lightly hydrogenated products led W. to assume that considerable isomerization of a-eleostearic acid takes place. Analyses of samples confirmed this. Conclusion: a-electearic acid glycerides of wood oil are isomerized to B-eleostearic acid glycerides during the course of hydrogenation." From C. A.

Yei, K. K.

CHEMISTRY OF TUNG OIL.

Rev. Chem. (Japan) 4, 92-104, 145-54 (1938)*; C. A. <u>32</u>, 8803 (1938). "A review." From C. A. (h) Use in Paints, Varnishes, Enamels, etc.

Anonymous

TUNG OIL IN CHINA.

J. Soc. Arts <u>48</u> (2466), 307 (1900); J. Soc. Chem. Ind. <u>19</u>, 359 (1900). "The chief use of tung oil in China is for the preparation of a standard paint. When boiled it is said to make one of the best drying oils. It is extensively used in varnishing with the Ningpo varnish, "t'si," i.e., the dried sap of the varnish tree (Rhus vernicifera), a good coating of which, it is stated, will resist considerable heat without leaving a mark, and will last for years. In order to give body and lustre to the paint, powdered galena and other ores are mixed with the oil." From J. Soc. Chem. Ind.

Anonymous

USE OF WOOD OIL IN THE MANUFACTURE OF VARNISHES. Painters Magazine, Oil and Colourmans J.; Chem. Rev. Fott- u, Harz-. Ind. 9, 287-8 (1902); Corps gras ind. 1903, 6 (July 15, 1903). Wood oil is used in copal varnishes to the extent of 5 to 10% (total oil basis) and in larger amounts when rosin is used. A wood oil substitute can be prepared by boiling for several hours at 140-150° C. wood oil (100 parts), linseed oil (20), Mn resinate (1), PbO₂ (0.5) and drier (2), then diluting with turpentine (8-16). For a varnish, use the above mixture (35), hardened rosin (35), turpentine (25) and a liquid drier (5).

Anonymous

MANUFACTURE OF VARNISH FROM CHINESE WOOD OIL.

Rev. prod chim. 5 (19), 293*; J. Soc. Chem. Ind. 26, 1404 (1902). "Wood oil is not suitable to replace linseed oil in the preparation of varnish, but only as an adjunct to impart solidity and hardness to the product. In no case should wood oil be heated above 160° C., or it will be permanently altered in character. For copal or gumresin varnishes, the proportion of wood oil must not exceed 5--10 per cent of the total oil taken, but for resin varnishes this amount is insufficient. For example, 45 kilos. of hardened resin are mixed with 54 litres of boiled linseed oil (containing a certain amount of driers), and heated to 140° C., at which stage 9 litres of wood oil are added. The temperature must be kept below 150° C., and after removing the varnish from the fire, it may be clarified with turpentine spirit, etc., as usual.

Another method is to heat together for several hours, at 140⁻⁻ 150° C., a mixture of: wood oil, 100 parts by weight; linseed oil, 30; manganese resinate, 1; red lead, 1/2; driers, 2 parts; the product being clarified by the addition of 8 parts of turpentine spirit in summer, or twice that quantity in winter. For resin varnish, 35 parts of this product may be mixed with an equal amount of hardened resin, 25 parts of turpentine spirit, and 5 parts of pale liquid driers. The resulting varnish may be used to mix with ordinary linseed oil and resin varnish--to an extent not exceeding 30 per cent of the oil in the latter, or the varnish will crack. The wood oil is freed from the contained moisture by a preliminary heating." From J. Soc. Chem. Ind. Anonymous

VARNISHES FROM WOOD OIL AND ROSIN.

Drugs, Oils & Paints 33, 192-3 (1918); C. A. 12, 316 (1918). "A review, with formulas and an outline of practice and control of wood oil varnish manuf." From C. A.

Anonymous

CHADELOID COMPANY DEVELOPED NEW VARNISH. CHLORINATED RUBBER AND CHINA WOOD OIL ARE PRINCIPLE CONSTITUENTS.

Paint, Oil Chem. Rev. 84 (5), 10-1 (Aug. 4, 1927).

Varnishes of good water resistance and flowing qualities can be made from chlorinated rubber and tung oil provided highly chlorinated rubbers are used with thoroughly heat treated tung oils and chlorinated rubbers of lower chlorine content are combined with tung oil oxidized and polymerized to a lower degree. Otherwise unstable, opaque solutions result. (Cf. patent by N. Boehmer.)

Anonymous

THE USE OF WOOD OIL IN THE PRODUCTION OF VARNISHES Paint Varnish Production Mgr. 15, 10,12,14 (Aug. 1936); C.A. 30, 6584 (1936).

"A review covering the uses of wood oil and certain substitutes in varnish making. The substitutes include oiticica oil, dehydrated ricinus oil called Synourin, blown linseed oils, chlorinated rubber, phthalic acid resins and benzylcellulose." From C. A.

Anonymous

PROPERTIES OF CHINAWOOD OIL VARNISHES COOKED AT DIFFERENT TEMPERA-TURES. C.-D.-I.-C. CLUB.

Am. Paint J. 21, Convention Daily 8, 23 (Nov. 18, 1936)*; C. A. 31, 558 (1938).

"Varnishes were prepd. and heated to different temps. between the limits of 232° and 288°. Heating and cooling curves are shown and phys. properties are tabulated. It is concluded that: it makes no appreciable difference at what temp. a varnish of this type is cooked providing the same body is obtained; it makes a much greater difference if the same varnish is cooked to a different body at the same temp." From C. A.

Anonymou s

SWING TO TUNG VARMISHES FORSEEN IN INDUSTRY.

Tung World 2 (7), 5, 19 (Nov., 1947).

A brief discussion of tung oil varnishes and of the merits and availabilities of various varnish oils and resins.

. . . .

Anonymous

TUNG-SOY HOUSE PAINT DEVELOPED.

Tung World 2 (12), 12, 26 (1948).

A brief description of the manufacture of a batch of house paint in a Gulfport, Mississippi, plant. Aalst, A. van

PAINTING OF BRIDGES OF THE NETHERLANDS CANAL SYSTEM. Congr. tech. intern. ind. peintures et inds. assoc. 1, 240-2 (1947); C.A. 43, 6835 (1949).

"Paints for steel bridges are based on linseed stand oil of viscosity 40 to 50 poises. A little bodied tung oil is added for the final coat. The painting system for bare steel consists of 4 coats, pigmented thus: (1) red lead, (2) red lead, iron oxide, (3) white lead, zinc oxide, (4) either chrome green and Bremen green or aluminum powder, graphite, and micaceous iron oxide. Formulas are given. Surfaces not exposed to sunlight receive only coats 1 and 2 followed by 2 coats of bituminous paint. Satisfactory protection for 6 to 8 years is obtained." From C. A.

Ahrens, E.

CONCRETE PAINTS.

Drugs, Oils & Paints 30, 327 (1915); C. A. 9, 1125 (1915).

"A concrete coating should be made from an unsaponifiable vehicle and curable pigments, ZnO predominating. Linseed oil paints are not recommended. By treating certain gum resins with solvents or with hot caustic alkali, the portion that would be affected by the alkali in the concrete is removed, and the residual product will give a durable vehicle. Heated wood oil dries to a tough elastic film in the presence of H₂O and is indurated against lime. A mixt. of ZnO with CaCO₂, asbestine or other inert pigments is recommended." From C. A.

Alb, Herbert

SPECIAL-EFFECT COATINGS.

Farbe u. Lack 54, 209-10 (1948); C. A. 43, 420 (1949).

"A review of frosted paints, crystal lacquers, wrinkle paints, crackle lacquers or paints, spatter, hammer, and web finishes." From C. A.

A number of these coatings contain tung oil as a primary ingredient.

Andes, L.

RUST-PREVENTING PAINTS.

Z. angew. Chem. 1902, 25-32.

No simple coating with linseed oil, wood oil, prepared oil, or spirit varnish protects iron sufficiently against weather but a good oil paint composed of a well prepared oil and an inert pigment is sufficient. With the exception of red lead in a prepared linseed oil all other coatings, including those made with wood oil, were destroyed by water in a short time.

Arndt, Willy

WOOD DIL, WOOD OIL VARNISH AND WOOD OIL LACQUER.

Kunststoffo 19, 57-9 (1929); C.A. 24, 1233 (1930).

"A general discussion of these materials including a brief review of their properties." From C. A.

"The enamels manufd. in Germany for export to the tropics are considered generally unsatisfactory because of chalking, blistering and particularly the long-remaining stickiness of the films resulting from the high humidity, the high temp. and the beating rain occurring in the tropics. In order to investigate the reason for this a series of Congo gum, limed rosin and ester gum varnishes were prepd. with the use of linseed oil, thick oil and (for ester gum only) wood oil as bases. Practically all the varnishes were unsuitable for application on tropical wood, primarily because of lasting stickiness. Films on black plate dried normally. The stickiness of the films and the resulting decrease in lasting quality increased with the sp. gr. of the wood and with increasing content of extractive substances (tannic acid). Brazilian woods are furthermore strongly permeated with rosin pockets which, because of their high content of volatile substances, tend to resoften the films. Enamels manufd. in the U. S. that had been satisfactory were made from artificial resins. Expts. with Albertol 111 L gave satisfactory results, similar to the American products, when a certain ratio of oil to resin was maintained. Copal, rosin and ester gum enamels could be employed when an Albertol primer was used. For enamels to be used in the tropics a Pb-Mn drior is most satisfactory. For white enamels it is recommended to substitute part of the Albertol with dammar, fused at 300°, but after-yellowing cannot be avoided even when pure linseed oil, stand oil or wood oil bases are used. Protective paints for concrete and iron should be prepd. from high-grade asphalt, Albertol and linsed cil only." From C. A.

Arnold, Hans

THE BODYING OF ZINC-WHITE ENAMELS.

Farben, Lacke, Anstrichstoffe <u>3</u>, 95-104 (1949); C. A. <u>43</u>, 5202-3 (1949).

"All stages of bodying or gelation, settling, and skinning are shown by 104 samples of pure ZnO enamels which had been stored 13 years, even though they were all made with 97-100% pure ZnO (max. of 3% TiO2), stand oil, and turpentine in the "classical" ratio of 2:2:1. Successive extn. of a stand oil (viscosity, 67 poises), in special apparatus, with 70% MeOH, 1:1 70% MeOH-EtOH (2 fractions), 1:1 MeOH-EtOH, EtOH, Me_CO (2 fractions), 70/30 Me_CO-"normal benzin" (3 fractions) brings out 10 fractions ranging from 3 to 1600 poises. These fractions are grouped according to viscosity as follows: (1) 38.0%, 3-7.3 poises; (2) 22.5%, 30-60 poises; (3) 19.0%, 105-135 poises; (4) 20.5%, 1500-1600 poises. Stand oils thus consist of a small fraction of high-polymeric dispersoid (which gels at once on heating to 100°, and flocculates in "benzin"), hemicolloid of medium viscosity acting as a soln. promoter, and low-polymeric material acting as a dispersant. The MeOH fraction is rich in fat acids. ZnO is compatible with the fractions (1) to (3), but gels (4). Stand cils bodied at low temp. and not pushed too far have been stored 20 yrs. without change; those bodied above 300° and

cooled or chilled rapidly, those pushed nearly to gelation and chilled with unpolymerized oil, and those in which linseed oil and chinawood oil were bodied together gradually become incompatible with ZnO. In such over-polymerized oils an unstable system exists in which there is too much of the high-polymeric dispersoid (or isocolloid) without enough of the hemicolloid soln. promoter. ZnO prepns. differ greatly in sorption, depending upon the size of aggregates, particle size and shape and amt. of H_O and CO2 taken up before calcining. Selective sorption is capable of upsetting the balance in an unstable stand oil. In soaps of high-polymer acids which thicken the vehicle suspend the ZnO particles loaded by sorption, producing a rubbery gel. If such soaps are absent, the ZnO particles will settle out; where the soaps form too slowly, settling followed by gelation may occur. The effects of thinners, flow promoters (benzoic acid), driers, anti-skinning agents, milling temp., and mixing procedures also are discussed." From C. A.

Arnold, R. H., and Frost, L. E.

INSULATING VARNISHES.

Elec. Mfg. 10 (4), 39-40 (October, 1932); C. A. 27, 433 (1933). "Methods of testing insulating varnishes are described. A varnish that can be used with a min. of solvent is preferable. The wire enamels in most general use have a China wood oil base combined with a small percentage of linseed, and varying amts. of fossil resins." From C. A.

Assheton, E.

· ANTICORROSIVE FAINTS. I.

Paint Manuf. 6, 242-4 (1936)*; C. A. 30, 7361 (1936).

"A discussion of rusting of iron and steel work, the types of anticorrosive paints and their application. Rust-preventing paints are classed as: (1) non-drying grease paints and (2) drying paints. Oil-sol. PhOH-CH₂O rosin-modified synthetic resins combined with wood oil are rapidly replacing linseed oil as media for anticorrosive paint. Flexibility and adhesion are the primary requisites of these paints. The newer oil-modified condensation products of polyhydric alcohols with polybasic acids offer a promising line of research." From C. A.

Backer, W.

RESIN OIL VARNISHES

Luck u. Farb. Rundsch. 1921, 113-4 (Aug., 1921); Chimie & industrie 7, 542 (1922); C. A. 16, 1874 (1922).

"Brief description of the following varnishes: copaiba resin; pistachio (Pistacia terebinthus); brewery pitch mixed with resin oil and castor oil; resin oil and wood oil; betulin from birch bark; birch tar; waste from the manuf. of corks from birch bark. Betulin is subjected to a special preliminary treatment at 350-70° under reduced pressure in an atm. of CO₂." From C. A. Baltimore Paint & Varnish Production Club

STUDY OF THE RELATIONSHIP BETWEEN THE PROPERTIES OF ESTER GUM-WOOD OIL-LINSEED OIL VARNISHES AND THE VISCOSITY OF THE LINSEED OIL COMPONENT.

Natl. Paint, Varnish Lacquer Assoc., Sci. Sect., Circ. <u>546</u>, 327-32 (1937); C.A. 32, 6889 (1938).

"Varnishes of 25 gal. wood oil and 5 gal. linseed oil were made in which the only variable was the viscosity of the linseed oil. This was 0.6, 13, 30, 110 and 650 poises. Water and alkali resistance, color retention, luster, nonpenetration and pigment suspension increased with increasing viscosity of linseed oil. Color, drying time, moisture absorption, dielec. strength, hardness, kauri reduction and skinning were not affected. The optimum viscosity appears to be 110 poises (No. 5 Litho oil)." From C. A.

Baltimore Paint & Varnish Production Club

EFFECT OF LINSEED OIL VISCOSITY OF VARNISH.

Am. Paint J. 22, Convention Daily 13, 14-15 (Oct. 26, 1937)*; Paint, Oil Chem. Rev. 99 (23), 80-4 (1937)*; C. A. 32, 1952 (1938).

"A continuation of the study of bodied linseed oils. Five ester gum varnishes of 30-gal. length (25 tung, 5 linseed) were studied with the linseed oils of different viscosities being the only variable. The exptl. data are tabulated and the following conclusions drawn: (1) The viscosity of the linsed oil component is a factor materially affecting certain important properties of these varnishes; increased viscosity tends to cause improvement in waterresistance, alkali resistance, color retention, luster, nonpenetration and pigment suspension; (2) except for brushability uncooked varnish linseed is undesirable for use in varnishes; (3)the optimum viscosity is approx. 110 poises: (4) the greater resistance to penetration imparted to varnishes by the heavier linseed oils points to their use in primer-sealer liquid formulation or in dealing with any problem requiring min. penetration; (5) improved color retention is obtained by the use of the heavier bodied oils: (6) the extremely viscous nature of the heavier linseed oils did not materially affect the viscosity of the finished varnishes; (7) with varnishes contg. both tung and linseed oils, the parts played by varnish acidity in producing livering with basic pigments depends largely on the degree of polymerization of the tung oil." From C. A.

Baltimore Paint & Varnish Production Club

BEHAVIOR OF CERTAIN OIL-RESIN COMBINATIONS. Natl. Paint, Varnish Lacquer Assoc., Sci. Sect., Circ. 604,

375-85 (1940); Abstract Rev. No. 64, 10; C. A. 35, 3464 (1941). "Varnishes were made with tung, oiticica, linseed, perilla and dehydrated castor oil and a proprietary synthetic oil with limed rosin, ester gum, modified phenolic and 100% phenolic resins. The varnishes were made in 15, 25 and 50-gal. lengths, with 2 drier combinations. The varnishes were tested for alkali and cold water resistance, color kauri reduction and outdoor durability. Increased cobalt reduced the drying time but impaired the water and alkali resistance and durability. In 50-gal. lengths the softer oils remained tacky for some time but were satisfactory in the shorter lengths. Dehydrated castor oil has the best outdoor durability and oiticica the poorest. A mixt. of the two would probably be better." From C. A.

Barghoorn, E. S.

USE OF PHENOL-FORMALDEHYDE AND VINYL RESINS IN SEALING LIQUID MOUNTING MEDIA ON MICROSCOPE SLIDES.

Science 106, 299-300 (1947); C. A. 42, 1449 (1949).

"Phenolic resins, especially p-phenylphenol formaldehyde (1) contg. tung oil and a metallic scap as an oxidizing agent, make satisfactory resins for prolonged sealing of noncorrosive and certain corrosive liquid media on slides. I has the sirupy consistency of a thick oil; when dried it is exceedingly hard, extremely adhesive to glass and inert to alcs., hydrocarbon solvents, halogenated hydrocarbons, and mineral acids. Vinyl resins were glasslike in appearance but sol. in a wide range of org. solvents. A vinyl acetate resin (II) was useful as a scaling compd. but was inferior to I. I and II are produced by the Bakelite Corp., New York City." From C. A.

Bearn, J. G.

VALUABLE FORMULAE AND DATA ON OIL VARNISH AND SOME HISTORY.
Paint Varnish Production Mgr. <u>34</u>, 20-7, 45 (Nov., 1930).
The early history of varnish is touched upon and present-day varnishes are classified according to end use and components.
For each type of varnish one or more formulas are given. A number of these contain wood oil. Eleven common defects of oil varnishes are listed together with their causes and methods of prevention.

B. gives manufacturing methods for linseed oil-copal resin varnishes and for wood cil-rosin (or rosin ester) varnishes.

Behr, Otho M.

INFLUENCE OF "STEARINE" ON HEAT FOLYMERIZATION OF SARDINE OIL. Ind. Eng. Chem. 28, 299-301 (1936); C.A. 30, 2785, (1935). "Substitution of sardine oil for all of the linseed oil and part of the China wood oil in making synthetic resin varnishes is suggested." From C. A. (abridged).

Bolotin, A. A., and Stankevich

VARNISHES FROM TUNG OIL AND ARTIFICIAL COPAL. Byull. Obmena Opytom Lakokrasochnoi Prom. 1939 (1), 26*, C. A. 34,5683 (1940).

"Tung oil and copal wore heated at 150-70°. The viscous product was dissolved in solvent naphtha and coal oil. These varnishes dry at 20° in 5-8 hrs.; a shiny waterproof film is obtained. They cannot be dried at elevated temps. owing to excessive yellowing." From C. A.

Bottler, Max.

GERMAN VARNISH MAKING.

Authorized translation with notes on American varhish and paint manufacture by A. H. Sabin. John Wiley, New York, 1912; pp. 314-315. Proceduros are given for the manufacture of varnishes from tung

Bruyn, C. A. Lobry de

RESULTS OBTAINED BY REGULAR INSPECTION OF PAINTED IRON STRUCTURES AND TEST PLATES.

Verfkroniek 11, 49-52 (1938); C. A. 32, 9524 (1938).

Comparisons were made of several media including a linseed oiltung oil standcil.

Butler, W. H.

RESIN EMULSION PAINTS, THEIR NATURE, ADVANTAGES AND PRODUCTION. Paint, Oil Chem. Rev. 105 (1), 10-12, 14 (1943) C.A. 37, 1880 (1943) "Polymerization of T part of oil-reactive ester resin, as represented by that based on dicycloheptenedicarboxylic acid, with 2 parts of China wood oil at 250° was complete (solid gel) after 10 min. as compared to 18 min. required for the resin alone and 27.5 min. for the oil alone." From C.A.

Carrick, L. L.

VEGETABLE OIL PAINTS.

J. Am. Oil Chemists' Soc. 27, 513-22 (1950)

The oils used in the manufacture of paints are reviewed with respect to their history, source, properties, heat treatments and uses. Oils discussed include tung, linseed, soybean, citicica, perilla, fish oil, tall oil, etc. Varnishes are made from tung oil with ester gum, hardened rosin, phenolic resins or alkyd resins.

Carver, W. L.

CHINA WOOD OIL IS USED AS BASE FOR BAKED COLOR ENAMEL. Automotive Inds. 50 (7), 324-5 (1924);

Substantial progress has been made in the past year in the development of improved finishing materials for automobile bodies. Hitherto the need for speed in production has made black the standard color. This article describes a noteworthy new development in color finishing which combines the sales advantages of brighter tints with the manufacturing advantages of the old process of applying black asphaltic base enamels. The base of the new material is tung or China wood oil, a drying oil which is extremely durable, of a high degree of penetration and adhesion, and capable of withstanding much higher temperatures than the usual drying oils.

Chicago Paint & Varnish Production Club.

A STUDY OF LIVERING AND ITS PREVENTION BY THE USE OF CATALYSTS. Am. Paint J. 17 (53B), 12-14 (1933); Am. Paint & Varnish Mfrs.! Assoc. Circ. No. 445, 459-69 (1933); Paint, Oil Chem. vRov. 95 (22), 80 et seq. (1933); C.A. 28, 347 (1934)

"The thickening of lithopone enamels contg. limed rosin-tung oil varnishes was proportional to the amt. of tung oil and acid value. Thickening was reduced by the addn. of small amts. of polar solvents, e.g., cellosolve, and by dibasic and tri-basic org. acids, the latter being more effective. An attempt to predict the thickening tendencies of varnish by means of Gardner's alkali increase test was not successful." From C. A. Dallas Paint & Varnish Production Club.

ELIMINATION OF CHINA-WOOD OIL FROM VARNISH FORMULATION. Official Digest Federation Paint Varnish Production Clubs No. 200 439-41 (1940); Brit. Chem. Abstracts 1941, B, II, 94.

"Varnishes to equal those from lightly-bodied tung oil must be quick-drying (a), water and alkali-resistant (b), and hard-drying (c). The use of oiticica oil satisfies (a) but the film is brittle and (b) is unsatisfied; mixing other oils with oiticica oil to reduce embrittlement greatly reduces (a). Dehydrated castor oil satisfies (b) but not (a) or (c). Using linseed oil with some of the newer phenolic resins, all conditions are reasonably fulfilled, cspecially when short oil lengths are chosen. Heavy body is not obtainable with any of these substitute products." From Brit. Chem. Abstracts.

Dean, R. L.

TUNG OIL RETURNS.

Tung World 2 (4), 14-6 (1947)

Formulations, cooking schedules and test results are given for a number of tung oil-Amberol (phenolic resin) varnishes. Because of its ability to dry fast to a hard film tung oil will be used in oleoresinous vehicles in greater quantities in the future.

Lerwael, A. H.

ALKYD RESINS .

Congr. tech. intern. inds. peintures et inds. assoc. 1947, 334-43; C.A. 43, 2463 (1949)

China wood oil is mentioned as one of the drying oils that may be used to modify alkyd resins. It is difficult to cause the two to react so to facilitate the reaction, China wood oil is generally used with rosin, rosin esters or phenolic resins.

Doel, H. V. D., and Hermann, F. J.

EXAMINATION OF PAINT RAW MATERIALS. VI. COMPARATIVE EXAMINATION OF SIX 100% AND TWO MODIFIED PHENOLIC RESINS. Contraal Inst. Materiaal Onderzoek Afdel. Verf., Circ. No. 37, 20 pp. (1947); C. A. 42, 770 (1949)

"Two alkylphenolic resins of low m. p. (58-72°) (I), 2 alkylphenolic resins of high m. p. (96-169°) (II), 2 arylphenolic resins (III) and 2 rosin-modified phenolic resins (IV) were compared. I and IV were sol. in toluene, II and III partially sol. In the prepn. of varnishes with tung, oiticica, and linseed oil I foamed, II and IV did not foam, and III foamed a little. I needed snorter cooking times than II, and the cooking times of III were equal to or longer than those of I. IV showed smaller cooking losses than I, II, or III; I gave the largest losses when cooked with tung or oiticica oil. Less solvent was required in varnishes made with IV. I and IV gave clear varnishes; the clarity of varnishes made from II and III was variable. The color of the varnishes varied with the oil used. With linseed oil, no increase of viscosity on storage was noted; I and IV gave very little increase, II more, and III most. The thickening on storage of enamels prepd. from leaded ZnO and the varnishes permitted no conclusion concerning the class of resin used or its acid no. In light-fastness tests on films of the enamels, I and II caused some discoloration, III caused much discoloration and IV a

Chopp, C. C. TUNG OIL OR CHINA WOOD OIL. Lrugs, Oils & Paints 32, 81-2 (1916); C. A. 10, 2646 (1916) "C. reviews methods of producing tung oil and discusses its importance in varnish manufacture." From C.A. Cleveland Paint & Varnish Production Club. A STULY OF ANTICXIDANTS AND ANTISKINGING AGENTS. Am. Paint J. 30 (6B) (Convention-at-Home Daily). 34-5 (1945) C. A. 40, 474 (1946) "Antioxidants are agents which retard the normal oxidation process of drying compns. The materials believed to possess antioxidant properties and tried out by the Comm. were: 50 gal. phenolic resin tung oil, 25 gal. ester gum tung oil, 25 gal. modified phenolic linsed oil. 40 gal. modified phenolic linsed oil and medium-oillength linseed-oil alkyd resin." From C.A. Clough, W. H., et al. CHICAGO CLUB STUDIES SOYBEAN OIL IN INTERIOR ENAMELS. Am. Paint J. 23, Convention Daily 16-17, 18-19, 21(Oct. 28, 1938); C. A. 33, 415, (1939) "Three types of resins employed in a study of the use of soybean oil in interior enamels were: (1) a 30% modified phenolic, (2) a 30% modified maleic and (3) an ester gum. Fortifying oils consisted of tung oil and perilla oil. Fifteen varnish combinations were made. Cooking of any one of the resins in combination with oil mixt. that contains over 50% soybean oil cannot be recommended. Combination of tung oil and soybean oil are good. Maleic resins react quickly with soybean oil and the other fortifying oils to produce a good body and good color. Tabular results indicate that calcg. the values as to color. [show ester gum to be best and phonolics poorest]***. The enamels ranking first in color, brushability and drying were made from half tung oil and half soybean; maleic resins pigmented with both series of pigments were used." From C. A.

- 305 -

Coolahan, R. A.

TORNES IT .

Official Digest Federation Paint Varnish Production Clubs No. 133, 39-42 (1934); C.A. 28, 2550 (1934)

"Tornesit" is stable at temps. up to 100°; decompn. is not serious until 135° and at 150° it begins to char. "Hercolyn," chem. plasticizers, blown linseed oil and bodied tung oil are suitable plasticizers. Amberols, coumarones, alkyds, ester gums and dammar may be used with Tornesit. A wide range of pigments may be used. Tornesit coatings have proved successful in various places about a nitrocellulose factory." From C.A. little bleaching. No significant differences were found in skin formation and drying time of the varnishes with added driers, extensibility of baked films and hardness. Swelling tests with H₂O showed that in linceed and oiticica varnishes IV were inferior to the others; In other varnishes they were approx. equal; there was a slight decrease in swelling from I to II to III. Leaching tests were inconclusive. Varnish films made from IV were inferior in resistance to boiling H₂O. Except in tung oil varnishes IV imparted less resistance to aq. Na₂CO₃ than the others." From C. A.

Dooper, R., and Hermann, F. J.

DEHYDRATED CASTOR OIL. II. PROPERTIES OF VARNISHES PREPARED WITH DEHYDRATED CASTOR OIL. PROPERTIES OF PUTTIES PREPARED WITH DEHYDRATED CASTOR OIL.

Centraal Inst. Materiaal Onderzoek Afdel. Verf, Circ. No. 51, ' 16 pp. (1948); C. A. 43, 372 (1949)

"A series of long-oil (I) and one of short-oil varnishes based on tung oil (II), bodied linseed oil (III), and two types of modified phenolic resin were prepd.; in some II and III were wholly or partially replaced by two types of bodied dehydrated castor oil (IV). Data on cooking times and conditions are given; replacing II by IV increased cooking time, but replacing III by IV resulted in no change. The oil used had no influence on the quantity of thinner that must be added to give a viscosity of 3 poises. All varnishes, except some I made with IV were clear. For varnishes with 0.3% Fb and 0.0 3% Co drier (based on oil) there was little difference for either series in speed of setting to touch; in through-drying (det'd by touch and pendulum method) the bils were equivalent except for tackiness in which IV was inferior. There was no difference in either series in extensibility, sanding properties, and skinning. In H2O absorption replacement of II by IV was unfavorable, that of III by IV favorable. There was no difference in leaching by H2O for either series. In resistance to 5% ag. Na₂CO- soln, a combination of II and IV was best. A plan for outdoor exposure tests is given. The sample of IV having longer drying time gave varnishes of better color, greater tackiness, greater H₂O absorption and inferior resistance to Na2CO3 compared with the other sample of IV; there was not difference in behavior during cooking. Futties were prepd. from chalk and linseed oil, two samples of dehydrated castor oil (V) or a mixt. thereof, with driers added. Putties made with V required more oil and wrinkled more; there was no difference in working qualities." From C. A.

Lrinberg, A. Ya., and Netshayeva, L. P.

AN IMPROVEMENT IN THE TECHNOLOGICAL PROCESS FOR PREPARING RAPIDLY DRYING CRESOL ALKYD LACQUERS.

J. Chem. Ind. (U.S.S.R.) 13 (14), 9-13 (1941); C.A. <u>38</u>, 3858 (1944). "The solm. of crosol-CH₂O condensation product is mixed in the cold with the alkyd base which contains 57.2% of a mixt. of linseed and wood oil. The best solvent is a 1:4 mixt. of BuOH and turpentime for a general painting lacquer. For a lacquer for spraying, it is best to use toluene with 3% rectified spirit. Fused metal cleates are used as siccatives." From C. A. Drofman, R. E.

WASHABLE DISTEMPER FORMULATION.

Paint Manuf. 7, 12-13 (1937); C. A. 31, 1641 (1937)

"The relation of the pigment, oil and water is outlined, and a method of dotg. the most economic grinding conditions is briefly indicated. The formulation of the eil phase is considered from the point of view of polymerization. A typical formula based on these views shows: pigment 100 parts, aq. phase 45 parts, oil phase 20 parts. The aq. phase contains glue 3 parts, casein 1.5 parts, borax 0.25 part, soft soap 0.75 part, lysol 1.5 parts and water 38 parts; the oil phase contains esterified copal 4 parts stand oil 4 parts, tung oil 2 parts and linseed oil 10 parts. The esterified copal should be dissolved in the stand oil and heated to 272° and kept at this temp., while the remainder of the oils are added at 45 min. intervals and the heating carried on until the varnish is thick enough to be readily emulsified with the app. available." From C. A.

Dubosc, A.

WOOD OIL VARNISHES.

Pointures, pigments, vernis 5, 527-8 (1928), C.A. 23, 4087 (1929)
 "On suitably cooking the ingredients an increase in the
proportion of wood-oil in a varnish dets. an increase in the
durability, without which it would be necessary previously to
harden the resin with lime. Directions are given for the making
of wood-oil varnishes for various purposes. For cheap varnishes a
certain amt. of wood oil can be replaced by soy-bean oil. The addn.
of Co drier not only increases their drying properties but also
clarifies them. For absolutely white varnish, it is advised to use
zinc resinate pptd. in the oil and treated with a small quantity of
Co drier." From C. A.

Fahrion, W.

ANALYSIS AND CHEMISTRY OF FATS IN 1907,

Z. angew, Cham. 31, 1219-28 (1908); C.A. 2, 2457-8 (1908) Reference is made to the opinion of Guedras that China wood oil is unsuitable for varnish manufacture.

Fancutt, F., and Hudson, J. C.

PROTECTION OF SHIPS' BOTTOMS AND THE FORMULATION OF ANTICORROSIVE COMPOSITIONS.

J. Oil & Colour Chemists' Assoc. 30, 135-62 (1947); C. A. 42, 2781 (1948).

"A systematic study of the formulation of paints or anticorrosive comps. for use on ships' bottoms is reported. Pigments studied were red lead, white lead, PbSO4 (basic), Burntisland red, barytes, graphite, Al, red oxide, ZnO, mineral black, Zn dust, BaCrO₄, witherite, ZnCrO₄ Zn tetrahydroxychromate, chromated Zn oxide, and lithopone. These were formulated into a total of 77 paints. Vehicles used in formulations were: Synthetic resin media including modified phenolic resin with stand oil; modified cresolformaldehyde resin with stand oil; alkyd and Zn resinate; British and American coumarone with litho varnishes; oleo resinous varnish media including litho varnishes with lime-hardened resin, Congo ester, Congo ester and Paraffin wax, Congo ester and zinc resinate; bituminous media; and sundry media including chlorinated rubber, shellac, and lanolin. Best pigments include basic Pb sulfate, Zn chromate, Ba chromate, mixed red lead and white lead, and Zn tetrahydroxychromate. Best media were chlorinated rubber, coumarone and litho oil, modified phenolformaldchyde and litho oil, and a 100% phenolic with tung oil and linseed oil. Most satisfactory formulation uses pigment compn. of basic Pb sulfate 40 parts, white lead 20 parts, Burntisland red 20 parts, and barytes 20 parts; in a vehicle of modified phenolic (Bedesol 66) 21.25 parts, heavy litho oil 42.5 parts, naphtha 35.40 parts, Pb naphthenato 0.68 parts and Co naphthenato 0.17 parts. Some of the compns. contg. Al showed better results than the above compn." From C. A.

Fancutt, F.

PAINTING AS IT AFFECTS THE RAILWAYS. J. Oil & Colour Chemists' Assoc. 12, 299-310 (1929)*;C. A. 24, 1232 (1930)

"The experience of the London, Midland and Scottish Railway Co. in painting rolling stock, bridges, stations, etc., is briefly reviewed. Much paint is applied by flowing while but little is sprayed. A quick drying coating for freight cars is prepared from suitable pigments with a vehicle made by adding 10% ZnO to a hot mixt. of linseed and tung oils, with lead and cobalt linoleates as additional driers." From C. A.

Faucett, P. H.

THE USE OF RAW AND TREATED OILS IN LACQUER.

Paint, Oil Chem. Rev. 96 (10),20-1 (1934); C. A. 28, 4253 (1934) "Oils, both raw and processed, are relatively low-cost materials that impart valuable properties to nitrocellulose lacquers. A table of properties is given for lacquers prepd. with various common fish and vegetable oils." From C. A.

Faucett, P. H.

CHINA WOOD OIL AND LACQUERS. Paint, Oil Chem. Rev. 100 (10), 20, 22, 24-9 (1938); C.A. 32, 8168 (1938).

"Various practical suggestions and formulas are given for dispensing with or decreasing the amt. of tung oil in protective coatings without impairing their properties. A lengthy discussion is given of how to use very simple, inexpensive app. to formulate and test various types of patent-free lacquers, sealers, etc., from com. nitrocellulose solns. made by sorting old movie films and dissolving in appropriate solvents." From C. A.

Flood, W. E., Booth, D. E., and Beisier, W. H.

CHINA WCOD OIL IN LACQUER I.

Ind. Ing. Chem. 20, 609-11 (1928); C. A. 22, 2671 (1928).

"China wood oil, raw, heat treated and combined with ester gum was incorporated in nitrocellulose lacquers, film properties were studied and exposure tests made. Lacquers contg. the oil were more durable than corresponding samples without oil." From C. A. Fonrobert, Ewald

RAPID DRYING VARNISHES.

Peintures, pigments, vernis, July, 1930; Paint Varnish Production Mgr. 25 (Mar., 1931) (abstract).

The author describes briefly the use of Amberols and a method of the manufacture of quick drying varnishes. Heat thirty-five parts wood oil to 260° C. and draw from fire, temperature goes to 280° C., then add 15 parts of bodied oil, part linseed, part Chinawood. Continuo heating at 260° to correct body. Finished product shows compatibility with synthetic resins and linseed and wood oil.

Fonrobert, E.

TUNG OIL AS RAW MATERIAL FOR VARNISHES AND SYNTHETIC RESINS. Farben-Chem. 7, 5-10, 49-54 (1936); Brit Chem. Abstracts 1936, B,607 "A lecture."

From Brit. Chem. Abstracts.

Fonrobert, E., and Brückel, K.

VARNISHES FOR THE TROPICS.

Fette u. Seifen 44, 432-4 (1937); C. A. 32, 1122-3 (1938)

"The improved resistance to tropical weathering obtained by using Albertols or tung oil or both together when formulating linseed oil varnishes is emphasized." From C. A.

Fronrobert, E., Holdt, C. P., and Wilborn, F.

AMERICAN AND GERMAN METHODS OF PREERING ALBERTOL TUNG OIL VARNISHES. Farbon-Ztg. 39, 89-90, 113 (1934); C. A. 28, 2925 (1934)

"The German method of prepg. albertol tung oil varnishes consists in thickening the oil at about 280°, subsequently dissolving the resin. The American practice consists in heating the oil and resin together throughout the procedure. The former method gave varnishes of paler color, lesser skinning tendencies, lower n, better flow and harder films (because of thinner films). The latter method gave varnishes of lesser wrinkling when baked, better gas proofness, more resistance to alkalies and to hot H₂0." From C. A.

Fonrobert, Ewald

TUNG OIL AS A RAW MATERIAL FOR VARNISHES AND SYNTHETIC RESING. III CONCLUSION.

Paint Manuf. 6, 45-8 (1936); C. A. 30, 3259 (1936)

"A review of the extensive uses of tung oil in varnish making and a word for oiticica oil as a valuable substitute. This oil is now being produced in increasing quantities." From C. A.

Fonrobert, Ewald

TUNG OIL AS A RAW MATERIAL FOR VARNISH AND SYNTHETIC RESINS.
Peintures, pigments, vernis 13, 102, 163-7, 191-6, 204-10 (1936)
Similar to "Tung Oil as a Raw Material for Varnishes and
Synthetic Resins. I, II and III." Paint Manuf. 5, 364-7 (1935);
6, 4-7, 45-8 (1936)

Gardner, H. A.

AN INTERESTING FOREIGN SEED OIL

Paint, Oil & Drug Rev. 68 (27), 8, 23-4 (1919): C. A. 14, 640(1920)
"An excellent drying oil not yet used in the paint and varnish industry is "soft lumbang" oil from Aleurites trisperma, the same botanical species from which tung (Aleurites fordii) and true lumbang (Aleurites moluccana) oils are derived. Analytical results on two samples of this oil which G. expressed from the seeds are tabulated in comparison with results on the two latter oils (Cf. C. A. 11, 714; 12, 869.) This oil does not jelly on the Browne heat test (C. A. 7, 2315) and when mixed with 10% of a Pb-Mn drier, it dries to a perfectly clear film in 14 hrs. After using in making varnish, it produced a H₂O-proof film that dried almost as well as a similar varnish made with tung oil." From C. A.

Gardner, H. A.

METALLIC SOAPS IN LACQUERS. TUNG OIL IN LACQUER FOR EXTERIOR WOOD SURFACES. Paint Mfrs' Assoc. U. S. Circ. No. <u>267</u>, 3-4(1926). C.A. <u>20</u>, 1912 (1926)

"A note on the elongation and tensile strength of clear lacquers contg. Pb linoleate, Cu oleate and Zn linoleate. G. points out that exterior lacquers are less durable on wooden than on metal surfaces because of greater expansion and contraction in wood. The use of 20% bodied wood oil in a nitrocellulose lacquer is suggested." From C. A.

Gardner, H. A.

A STUDY OF THE EFFECT OF VARIOUS THINNERS FOR COLD-CUT AND HEAT-PROCESSED QUICK LRYING VARNISHES. Paint Mfrs. Assoc. U. S. Circ. No. 278, 90-7 (Aug. 1926); C. A. 20, 3353 (1926)

 $V \cdot H \cdot L V, 0000 (1920)$

"A comparison of varnishes made from (1) tung oil, synthetic resin cold-cut, (2) the same, heat treated, (3) tung oil, ester gum heat-treated. The addn. of toluene and gasoline to the thinners to speed drying while slightly effective often led to unsatisfactory film conditions. The phys. properties, drying, hot water tests and 5 months' exposure tests are tabulated." From C. A.

Gardner, H. A., et al.

1LLUSTRATED LABORATORY NOTES (PAINT AND VARNISH) Am. Paint Varnish Mfrs.' Assoc. Circ. No. 358, 1-73(1930). C. A. 24, 736 (1930)

"The durability of exterior house paints was apparently improved by replacing a portion of the raw linseed oil with bodied tung oil or spar varnish. The use of ZnCl₂ as a preservative for interior lumber in humid places adversely affects the paint applied to it. The use of trimetal primer on red cedar inhibits staining. Titanox contg. adsorbed H₂SO₄ settled more rapidly in a paint than titanox contg. adsorbed NH₃ or NaCH. Accelerated settling tests did not wholly agree. Wood rosin in ship bottom paints was equal or superior to gum rosin. "Soligen" driers while possessing better soly. are not, when compared on the basis of the actual wt. of metal, superior to the usual driers. A sample of Filchard oil possessed the following consts.: Wijs no. 191.1 sapon. no. 192.1, octabromide no. 32.7, np23 1.482. The storage properties of flat paint contg. natural whiting were better than those of paint contg. pptd. whiting. The use of phthalic anhydride in crystg. lacquers and of the mineral Jeffersite in plastic paints is suggested. Details are given of gloss oils contg. 2-14% of lime, on lacquers contg. rezyls and other resins, on varnishes prepd. with solvent-extd. Kauri and with a resin found in Utah coal. Accelerated testing equipment and a bubble viscometer testing frame in use at the Inst. of Paint & Varnish Research are

Gardner, h. A.

SOME PROTECTIVE COATING SYSTEMS OF INTEREST TO THE GAS INDUSTRY. Am. Paint Varnish Mfrs.' Assoc. Circ. No. 382, 167-86 (1931); C. A. 25, 3501 (1931)

"While alloys that resist soil corrosion have been developed, they are too costly for extended use in pipe lines. Special protective coatings for ordinary iron pipes must therefore be developed. In addn. to the usual requirements of coatings, such systems must not be deformed when in contact with the soil, must be easy to apply in the field, patchable in case of repairs to the lines, etc. An accelerated test used by G. consisted of burying the pipes in a tank of cinders and S, which were wet daily with a 1%soln. of H_2SO_4 . Every third day the tank was drained. A no. of systems which withstood such a test for 4 months are described. A low cost transparent temporary shop coating for pipes consisted of bodied oil 90 (tung oil 75, other oil 25), ZnO 10, thinned to dipping or spraying consistency. A novel coating device is described." From C. A.

Gardner, H. A.

OITICICA-OIL INVESTIGATIONS.

described." From C. A.

Paint Varnish Production Mgr. 14, (6) 16, 18, 30 (1936); C. A. 30, 5432 (1936)

"Fhenolic resin-oiticica oil varnishes are more durable than similar varnishes made with tung oil; ester-gum-oiticica-oil varnishes are inferior to corresponding tung oil varnishes. The different behavior is ascribed to a reaction of the former resin with the keto group in oiticica oil. This hypothesis was tested by causing oiticica oil to react with various pheonols used in the manuf. of phenolic resins, viz., cresol, phenol, p-tertamylphenol. Phosphoric acid catalyzes the reaction. The durability of ester-gum varnishes made with the treated oil was extended. Oiticica-oil varnishes are relatively free from skinning and gelling both during and after cooking. They are less waterresistant than tung-oil varnishes. Varnishes made with oiticica oil can be cooked at higher temps. than those with tung oil with subsequent freedom from gas checking. Wrinkling is less pronounced with oiticica oil and the oil can be mixed with other oils to produce nonwrinkle rapid-drying films. Oiticica oil is readily emulsifiable and the emulsions are suggested for flat wall paints. Its fat acids are suggested for use in waxes, polishes and antifouling paints. Present production exceeds 3000 mutric tons per year. Modern methods of extn. are yielding an improved product." From C. L.

Gardner, H. A., and Hart, L.P.

FIELD TESTS ON QUICK-DRYING HOUSE PAINTS. Am. Paint Varnish Mfrs.' Assoc. Circ. No. 374, 32-52 (1931) C.A. 25, 1104 (1931). "A preliminary report is made on exposure tests on a no.

of quick-drying house paints conducted at Gainesville, Fla. The vehicles included bodied tung-linseed oil mixts., glycerol phthalate compns., other synthetic resins and nitrocellulose lacquers. Formulation, spreading rates and comments on brushing properties. are given." From C. A.

Gardner, H. A., and Holdt, P. C.

THE ALKALI INCREASE TEST FOR TUNG-OIL VARNISHES. Paint Mfrs. + Assoc. U. S. Circ. No. 206, 25-34 (June, 1924) C. A. 18, 2815 (1924)

"If 10 cc. of 2.5 N NaOH is added to 200 cc. of varnish. stirred vigorously for exactly 2 min., and allowed to stand in a viscometer bath at 25° for 30 min., a big increase in viscosity takes place. In some case the mixt. becomes solid. This increase is measurable with linseed-oil varnishes, but is not nearly so great as with varnishes contg. tung oil; it is independent of the acid no. of the varnish, but appears to be a measure of the degree of polymerization of the oil during the manuf. of the varnish. The alkali increases of viscosities on some com. varnishes are tabulated. The test gives fairly reproducible results on different batches of varnishes made according to the same formula and process. Aging of the varnish for 30 days showed no great change in the results of the test. Increasing the amt. of drier in the varnish formula increased the viscosity of the untreated varnish, but did not appreciably affect the viscosity after treatment with alkali. The reaction which takes place may be due to withdrawal by the alkali of resin acid, which ordinarily keeps the polymerized wood oil from coagulating. or it may be due to changes in the colloidal nature of the varnish. Application of the test will probably give useful information for research and for checking the uniformity of successive batches in com. varnish manuf." From C. A.

Gardner, H. A., and Sward, G. G.

RECENT VARNISH EXPOSURES.

Am. Paint Varnish Mfrs.' Assoc., Circ. No. 410, 129-34 (1932); C. A., 26, 3682 (1932).

C. A.,26, 3682 (1932). "Various exposure tests in different localities of oleoresinous varnishes indicated the superiority of bakelite-tung oil varnishes. In one case, however, a 44-gal. ester gum-tung oil varnish contg. O.1% S showed pronounced durability. Varnishes prepd. with simultaneously formed bakelite and glycerol phthalate resins were not particularly durable." From C. A. Golden Gate Paint & Varnish Production Club

OIT ICICA OIL-ESTER GUM VARNISHES

Paint, Oil Chem. Rev. 97 (23), 72 (1935); Oil Paint Drug Reptr. 128. (22), 54 (1935) C. A. 30, 4700 (1936)

"Oiticica oil-ester gum and tung oil-ester gum varnishes were made in 15-, 30-, and 45-gal. oil lengths and tested for drying power, gassing, water resistance, etc. It appears that ester gum alone is not the proper resin to use where oiticica oil predominates in the varnish, as such varnishes are slow to dry, have poor waterproofness and reduced flexibility." From C. A.

Guedras, Marcel

THE INDUSTRY OF VARNISHES

Chom: Rov. Fott-u. Harz-Ind. 10, 287-288 (1903). A thorough review in which Wood oil is mentioned as a substitute for linseed oil.

Hafeli, John M.

TRAFFIC PAINTS, STUDY OF TYPICAL FORMULATIONS.

By Gum 18 (2), 3-6 (Oct. 1947); C. A. 42, 771(1949).

"A Short-oil, fast-drying, modified alkyd and a nonphthalic alkyd with a medium drying rate were compared to standard 20-gallonoil-length, modified-phonolic, China wood oil varnish in 5 white and in 5 yellow pigment blends commonly used. A nonreactive grade of ZnO was employed. The white paints contained 64-65% NV, pigment vol. 32-34%. The yellow paints contained 62-63% NV, pigment vol. 24-25%. Faints contg. ZnO were harder and firmer after a 24 hr. air dry, but tended to body during aging in the container. Yellow paint contg. varying proportions of lead chromate tended to be more viscous, particularly when reactive ZnO was used. Thirty prepd. paints were brusned on a macadamized road for observation. Paints contg. the most ZnO in each group were first to fail. After several months, color differences became pronounced; the paints formulated with Ti-Ba pigment (I) were degrees whiter. Silica and Silicate-bearing paints were cleaner than paints formulated with tale. The best color retention was exhibited when ZnO was used with I. The vellow paint made with ZnO displayed the best color retention. The short-oil, modified alkyd showed best all around properties." From C. A.

Hafeli. John M.

TUNG OIL: ITS PAST; PRESENT AND FUTURE.

By Gum 19 (5), 7, 10-13 (1948); Can. Paint & Varnish Mag. 22 (11), 36, 38, 40, 42, 62-3 (1948); C. A. 43, 419 (1949)

This review gives a picture of tung oil use from the point of view of a technical service man for a resin manufacturer. Since 1905-10 tung oil has been known to impart fast drying characteristics to paints, varnishes, and enamels, and to make the dried films hard and resistant to water and chemicals, Following World War I tung oil came to be considered essential for automotive finishes. The development of oil-modified alkyl and phenolic resins did not interfere with its markets since the tung oil was found desirable for incorporation into those resins. Luring World War II the armed services insisted on some tung oil in most of their protective coatings to insure fast drying and film durability. For the

future, the writer anticipates increased uses and improvements in the quality of the oil.

Hafeli, J. M.

THE USE OF DRYING OILS IN OLEORESINOUS VARNISHES.

J. Am. Oil Chemists' Soc, 27, 523-9 (1950)

The manufacture of varnishes is reviewed with a general discussion of the oils and resins used. Formulas are given for 13 types of varnishes. Of these, 11 contain tung oil. If it were more plentiful and cheaper, tung oil could be used to a much greater extent.

Hagar, I. D.

THE USE OF FIXED PAINT OILS OTHER THAN LINSEED. Drugs, Oils & Paints 35, 289-90 (1920); C. A. 14, 850 (1920). Tung oil is one of a large list of oils which has been tried as a linseed oil substitute. It is excellent for varnishes and for coatings used on cement and plaster. It has been less satisfactory as an outside white paint.

Hebberling, H.

FAST-DRYING LACQUERS OF SYNTHETIC RAW MATERIALS.

Oberflachentech. 11, 143-4 (1934); C. A. 28, 5689 (1934)

"New kinds of lacquers and varnishes are made of copal-like synthetic resinous substances with fast-drying wood oil. While natural copals can be mixed with oils only after a long boiling and melting process, the artificial products can be treated directly with linseed and wood oil. These lacquers are preferably used for inside purposes as they are not very resistant to sunlight, but resist well water and chem. actions. They dry in 4 hrs., but a longer time is better for durability." From C. A.

Hermann, F. J.

INFLUENCE OF TIME AND TEMPERATURE OF COOKING ON THE PROPERTIES OF 1:2 VARNISHES+ CONFAINING AN OIL-REACTIVE PHENOLIC RESIN AND TUNG OIL.

Centraal Inst. Materiaal Onderzoek. Afdel. Verf , Circ. No. 55, 11 pp. (1949)*; C. A. 43, 7238 (1949)

"A soln. (I) of 600 g. of a 100% phenolic resin and 1200 g. tung oil was made by heating at 180° 18 min. Half of I was heated to 230° for 15 min. under CO₂ and held at that temp; samples were removed at intervals; gelatinization took place after 100 min. The other half was similarly treated at 240°; gelatinization took place after 70 min. The "string test" does not indicate differences in the latter stages of the cook; the Me₂CO-insol. fraction (II) and viscosity (III) increase with increasing temp. and reaction time; the relation between II and III is independent of the temp.; the Me₂CO diln. test indicates the extent of reaction; n varies very slightly; color does not vary with temp. but increases with time. Varnishes adjusted to 3 stokes, contg. 0.05% Co drier (based on Co and oil), show increase in skinning and gelatinization with increasing cooking time; drying of the films improves irregularly with cooking time; for the dry films leaching by H_2O increases slightly with reaction time; H_2O absorption is the same except for the sample prepd. at 230° for 10 min.; H_2O resistance and outdoor performance are the same; alkali resistance increases with reaction time. From C. A.

Hermann, F. J., and Dooper, R.

OUT DOOR EXPERIMENTS WITH FINISHING PAINTS ON WOOD. Congr. tech. intern. ind. peintures inds. assoc. 1, 278-84 (1947) (in English); C. A. 43, 4491 (1949).

"The authors carried out 3-yr. exposure tests of various paint systems on Scotch pine panels. Fifty-one different pigmented finish coats were used. In comparing vehicles of finish coats in resistance to cracking and peeling, a bodied linseed oil-modified phenolic resin vehicle (80% oil; 20 % resin) was much inferior to the 3 others, viz., bodied linseed oil alone, pure phenolic resintung oil, and alkyd resin. These 3 were rated about equal. The alkyd resin vehicle provided the greatest resistance to chalking and the best appearance. In comparing white pigments of finish coats in resistance to cracking and peeling, PbTiO3 was excellent; nonchalking TiO2 was satisfactory; others tried were poor. Deterioration at 50° from the horizontal was somewhat more rapid than at 45°. Mildew formation was greatest when the pigment was PbTiOz or TiO, . Large proportions of ZnO, ZnS, chrome green, or Al prevented mildew. The nature of the vehicle did not affect the formation of mildew. In the colored finish coats, the best durability was given by iron oxides, chrome yellow, and Al. In mixed pigment paints, the durability did not exceed that obtainable from the best component used alone." From C. A.

Holdt, Charles

OITICICA OIL

Drugs, Oils & Paints 51, 191-2, 194, 196, 198 (1936); C. A. 30, 5060 (1936)

"A comparison with China wood oil varnish formulas and cooking procedures. A no. of varnish formulas and the cooking procedures are butlined where the oil consisted of: (1) 100% oiticica oil, (2) 100% China wood oil, (3) 50% oiticica oil--50% China wood oil. In general the varnishes contg. 100% oiticica oil took very little longer to body than those contg. 00% oiticica oil varnishes, while in some cases the time was shorter. Oiticica oil varnishes are more gas proof than similar China wood oil varnishes. Used in conjunction with China wood oil, oiticica oil reduces the gas resistance of the former. Oiticica oil varnishes are much superior in respect to gas resistance and storage characteristics, while China wood oil products are more water resistant and, in general, produce harder films." From C. A. Hornemann, C.

TYPES OF WOOD PRESENTING DIFFICULTIES IN VARNISHING. Ind.-Lack.-Botrieb 2 (15), 181-2*; Research Assoc. Erit. Paint Mfrs.' Rev. No. 28, 239 (1932)*; C. A. 26, 6162 (1932) "Certain woods present difficulties accordingly as they are hard and porous (mahogany, ash, elm, etc.), soft and porous (poplar), resinces (coniferous) or very dense and hard (teak). Primers for such woods should never contain fatty oils such as linseed or tung oils, because in resinces woods the oil combines with resin, and in very hard woods the oil merely remains on the surface; in porous wood the oil is liable to remain in the pores without thorough drying, and this is evident in the top coat. The best material to use is a good oil-free primer in a dil. form; this hardens the surface and insulates the resin in the wood." From C.A.

Hurt, E. F.

NON-EDIBLE VEGETABLE OILS.

Chom. and Druggist 152, 615 (1944); C. A. 39, 995 (1945). The origin and use of tung oil in paints are briefly mentioned.

Joachim, Benjamin

APPLIED PAINT AND VARNISH CHEMISTRY FOR THE CHEMIST AND THE LAYMAN. Am. Paint J. 19, 13, et seq. (Aug. 19, 1935)*;C. A. 29, 6773 (1935) "A discussion of the advantages of natural resin esters in combination with Synthetics. 100% PhOH varnishes have excellent resistance to weathering, chemicals and solvents, as well as speed of drying. The effects on the time of gelation of China-wood oil and of 75% China wood-25% linseed oil are indicated. Formulas are given." From C. A.

Johnson, H. M.

SYNTHETIC HOUSE PAINT FROM VARIOUS VIEWPOINTS.

Faint, Oil Chem. Rev., 93, (22), 10-20 (1932); C. A. 26, 4187(1932) "A synthetic resin house paint should have an orthodox odor, should age well, brush like an ordinary paint, set up quickly, weather by mild chalking and cost no more per unit area than ordinary paint. The change from a linseed-oil vehicle to a synthetic vehicle will come about slowly, especially for whites and tints. A vehicle composed of 80 parts raw linseed oil and 20 parts of a 25-gallon tung oil-phenolic resin varnish is recommended for quick-drying paints." From C. A. Jones, A.

WRINKLE OR CRYSTAL FINISHES.

Paint Manuf. 6, 382, 384 (1936); C. A. 31, 1233 (1937)

"The wrinkle finish is obtained by spray application, followed at once by a bake in a closed oven, gas-heated inside, at 66° to 240° for 1/2-2 hrs. depending on the specific finish recipe. The formation of the wrinkle depends on the quick formation of a surface film of processed wood oil by polymerization and oxidation. Bitumen- and synthetic-wrinkle finishes are briefly discussed and a few typical examples of synthetic wrinkle paints are given." From C. A.

.K., C.

THICKENING OF COPAL VARNISHES Farbon-Ztg. 18, 1, 1119-20 (1913)

C. K. agrees with Muchle that it is difficult to neutralize copals and that it can not be done as Mr. K. describes (Farben Ztg. 1913, P. 588). Varnishes that will not thicken after pigments are incorporated can be made by carefully melting copal with a "bottom" of rosin, cooking it for a few minutes longer, adding enough warm oil for "saturation" of the copal, raising the temperature to 320° C., removing the kettle from the fire, neutralizing the melt with ournt magnesia cooling it to 220° and adding driers. The blend of a properly preapred varnish with Stand oil (linseed, 85%; wood oil, 15%) will remain limpid.

K., M.

THICKENING OF VARMISHES WITH ZINC AND LEAD COLORS AND REMEDIES FOR IT.

Farben Ztg. 1913, . 588.

When acid resins like rosin and acid copals are used in varnishes the varnish should be neutralized with slaked lime, calcium borate or burnt magnesia (free from carbonate). Kauri, unless adulterated, is a safegaurd against thickening. Note by Editor of Farben Ztg.: Real neutralization and esterification are generally not feasible.

Kellam, R. I.

EFFECT OF CHINA WOOD AND FISH OILS IN OUTSIDE PAINTS. Am. Paint J. 17 (53^B), 16, 20; Am. Paint Varnish frs'. Assoc. Circ. No. 445, 477-80; Paint, Oil & Chem. Rev. 95 (22), 83-14 (1933), C. A. 28, 347 (1934)

"Various properties of paints prepd. with linseed, tung, fish (pilchard) oils and mixts. thereof are noted and tabulated. Fish oil imparts to paints elasticity, blooming, non-yellowing and nondiscoloration. Tung oil imparts gloss, a certain degree of shortness and yellowing." From C. A. Kemner, H.

TUNG AND OITICICA OILS AND THEIR MIXTURES WITH PERILLA OIL. Farbe u. Lack 1939, 171-172; Brit. Chem. Abstracts 1939, B. 629; C. A. 33, 9015 (1936).

"Tests with oil and varnish films containing Pb-Co drier show that replacement of 30-50% of tung or oiticica oil by perilla oil improves the brushability and flow without loss of drying time or H₂O-resistance." From Brit. Chem. Abstracts.

kemner, H.

TALL OIL IN THE COATINGS INDUSTRY.

Farben, Lacke, Anstrichstoffe 1. 20-1 (1947); C. A. 42, 8489 (1948). "Good coatings can be obtained from vacuum-dist. tall oil (av. acid no. 170) (1) by treatment with CaO or ZnO followed by esterification with suitable polyhydric alcs.; (2) by incorporation into alkyd resins; and (3) by reaction with China wood or oiticica oil followed by esterification." From C. A.

Kojevnikoff, N. N.

SLOW-DRYING OIL VARNISHES: THEIR FORMULATION+ PROCESSING AND PROPERTIES. II.

Official Digest Federation Paint Varnish Production Clubs No. 206, 244-53 (1941); C. A. 35, 5728-9 (1941)

"The low rate of bodying in slow-drying oils was attributed to insufficient acid concn. present in the drying oil coupled with the low rate at which the acid is generated during the slow processing of the oil. An attempt was made to det. if the bodying rate could be increased by an addn. of acid to the oil. As mineral and org. acids added to these sils cause discoloration. the acid concn. was increased by means of synthetic resins. The behavior of China wood oil was first tested with various resins. A series of 18 gal. varnishes was prepd. with resins whose acid no. varied from 6 to 170. All varnishes were prepd. in exactly the same manner, the cooking being carried to a similar end point of a heavy drip. From the comparison of resultant varnishes it was noted that the bodying rate of China wood oil was independent of the length of the oil in the kettle and of the acid value of the resin used. The bodying rate was detd. by the ratio of the total acid value of the resin to the total acid value of the oil. When the acid ratio was plotted against the bodying rate the latter increased with diminishing ratio, reached a min. at a certain ration and then decreased with further decrease in the acid ratio. For China wood oil the shortest holding time was at 2.75 acid ratio which was called the "optimum acid ratio" at which the bodying rate was the greatest and the varnish properties the best. Deviation from the optimum acid ratio caused slower bodying and interior properties. The acidity of the varnish was detd. by the acidity of the resin rather than the acidity of the oil. At the optimum acid ratio the acid value of the varnish was lower than that of the oil used. The acid ratio was detd. by dividing the total acidity of the resin by the total acidity of the oil, total acidity being the acid value multiplied by the g. of material used. A

comparison was made of the use of a resin of high acid value with China wood oil using the optimum acid ratio to calc. resin to be used. The bodying rate of the resultant varnish was the same. as were the acidity and drying properties. The behavior of alkalirefined perilla oil was then detd. It was found that the effect of the acid ratio was less pronounced than with China wood oil, the bodying rate was the same regardless of the ratio, and was reduced by the addn. of the resin. The acidity of the resulting varnish was independent of the acid value of the oil, and the effect of the acidity of the resin upon the acid value was negligible. The best results with alkali-refined perilla oil were obtained with resins of acid value of 120. Such results were obtained when the acid ratio was 19.7, deviation from which yielded varnishes of inferior properties. These findings led to the conclusion that every oil has an acid ratio at which the bodying rate is at its min., and the properties of the varnish obtained at that ratio appear to be more than satisfactory." From C. A.

Kolke, F.

NITRO-OIL OR COMBINATION LACQUERS

Farben-Ztg. 33, 861-2 (1927) C. A. 22, 3054 (1928)
 "The combination of nitrocellulose varnishes with oil
varnishes is discussed. Curves are given showing the limits of
compatibility of tung oil with 20% 1/2-sec. nitrocellulose solns.
in butyl acetate and in hexalin acetate." From C. A.

Kolke, F.

RECENT FINISHES.

Farben-Ztg. 35, 2569-70, 2618-9 (1930); C. A. 24, 6038 (1930)
 "The technology of recent novelty finishes, such as crackle
lacquer, wrinkle finish, etc., is reviewed." From C. A.
 Some of these finishes contain tung oil.

Kolke, F.

DECORATIVE FINISHES FOR PLASTICS

Gelatine, Leim, Klebstoffe 3, 19-26 (1935); C. A. 29, 4192 (1935) "Special finishes are classified by the effects produced upon drying; many of them result from phenomena that previously were considered defects in finishes. "Frost-flower varnish" is the oldest form of special finishes. It is a wood-oil varnish that can be thinned with turpentine and applied by brush or by spray. "Wrinkled varnish" is known also as fabric, shrinking or damask varnish. It is based on tung oil, applied by spraying without a priming coat, and usually dried in an oven between 50° and 150°. "Crackle lacquer" is usually a cellulose product that requires three coats, the second being applied before the first is completely dry. "Grain lacquer" is a quick-drying cellulose lacquer that must be sprayed. The effect is due to a high viscosity: The "Lymmato process" is covered by proprietary patents. The spraying equipment is adjusted to throw the coating material on the surface in a spotty, random distribution. Illustrations of the surfaces produced by these different finishes are included." From C. A. Kolln, H.

THE MANUFACTURING TREATMENT OF WOOD OIL

Farben-Ztg. 31, 920-1 (1926); C. A. 20, 1912 (1926)

"K. reviews the methods of plant treatment of wood oil for the production of varnishes and bodied oil." From C. A.

Kolln, H.

FLOOR VARNISHES.

Farbe u. Lack 1929, 52-3; C. A. 23, 1762 (1929)

"Many complaints of inferior floor varnishes are due to improper prepn. of the floor or to an insufficient period of drying. When time permits, an excellent finish is obtained with a zinc oxidestand oil enamel. Tung oil in small quantities may be added to accelerate the drying." From C. A.

Kopf, C. W., and Mantell, C. L.

MATURAL RESINS IN QUICK-DRYING TRAFFIC PAINTS. I.

Faint, Oil Chem. Rov. 102 (11), 7-8, 28-30 (1940); C. A. <u>34</u>, 7624 (1940).

II. THE EFFECT OF CHINA WOOD AND OTHER OILS IN QUICK-DRYING VENICLES.

Ibid. (12), 44-6, 48-9 (1940).

III. FORMULATIONS AND PERFORMANCE TESTS OF QUICK-DRYING VEHICLES. Ibid. (14), 9-11, 24-7. (1940)

"The effect of varying components in a widely used quick-drying spirit vehicle for traffic paints was studied. This vehicle is 35% Manila DBB (natural resin) and 65% solvent. The solvent is 15% raw tung oil, 17% butanol, 34% acetone and 34% denatured alc. Paints in which one component of this thinner had been varied were tested by stripping on a concrete road over which 800-1000 cars passed each day. Some tests were performed on a bituminous road. Best wear was obtained with softer resins. Of linseed, soybean, perilla, oiticica, fish, dehydrated castor and castor oils all but oiticica gave better wear than tung oil. Elemi gave a betterflowing paint. High pigment values give greater durability. Higher oil ratios prevent cracking of films, with the max. at 4:6. On bituminous roads addn. of alc .- insol. resins caused little bleeding and too great an oil content caused dirtying of the stripe. Raw tung oil is detrimental to the stability of this type of traffic paint." From C. A.

Kraus, A.

PLASTICIZERS FOR MITROCELLULOSE LACQUERS. XIII. THEIR SOLVENT POWERS. XIV. TRAIN OILS AS PLASTICIZERS.

Farbe u. Lack 1939, 493, 499, 505, 511, 529-30; C. A. 34, 6465 (1940). "Although the compatibility for nitrocellulose (1) of train oil is better than that of linseed and tung oils, it reduces the tensile strength of the films without increasing their elasticity; hence, like other drying oils, it is not a true plasticizer." From. C. A. (abridged). Lesser, M. A.

RECENT DEVELOPMENTS IN THE USE OF GLYCERINE AND ALKYD RESINS IN COATINGS.

Am. Paint J. 33, (19), 48-50, 52 (1949).

China wood oil is one of the drying oils used to modify alkyd resins made for coating purposes.

• •

Levinson, S. B.

TUNG OIL IN THE PAINT + VARNISH INDUSTRY. Tung world 2 (2), 8-11 (June, 1947) The manufacture and testing of tung oil varnishes are described.

Lewis, A. J.

COMPERATIVE DURABILITY OF SOYBEAN AND OTHER OIL VARNISHES. Paint, Oil Chem. Rev. 102 (9), 9-11 (1940); C. A. 34, 7631 (1940) "Soybean oil varnishes compare favorably with linseed, perilla and tung oil varnishes for durability. In general the cooking or bodying time is longer for soybean oil than for the other oils." From C. A.

Livache and McIntosh

THE MANUFACTURE OF VARNISH AND KINDRED INDUSTRIES. Scott Greenwood and Co., London, 1904, Vol. I, pp. 134-9 The source of wood oil, its intorduction into England, methods of using it in varnishes and the detection of adulteration of wood oil are discussed.

Loo, S. C.

TUNG OIL AND RECENT DEVELOPMENTS.

Inspection and Commerce (China) 4 (10), 19 (1933)

Although synthetic finishes are rapidly coming to the fore, tung oil will continue to find markets for the modification of phenolic resins and for use in oleo-varnishes which continue to be in demand because of their lower prices.

Loon, J. van.

FROP_RTIES OF PRIMING PAINTS

Verfkroniek 8, 70-4 (1935)*; C. A. 29, 7097 (1935)

"This is a preliminary report of work done to select the most suitable paint for iron from the various paints which can be prepd. from (a) the pigments, red ocher (I), various red leads and Zn chromate (II) and (b) the vehicles, linseed oil (III), heat-treated III, either alone or mixed with tung-oil stand oil and "waterproof varnish" and (c) nahptha for thinner." From C. A. (abridged) Loon, J. van

PURPOSE AND IMPORTANCE OF PRIMING PAINTS.

Chem. Weekblad 33, 345-51 (1936); C. A. 31, 4139-40 (1937)

"Natural and accelerated weatering tests on priming paints for Fe indicate the general superiority of red lead paints over Fe₉O₂ paints, but 10% of Fe₉O₂ can be included without detriment. Addn. of CaCO, can be included without detriment. Addn. of CaCO₃ is, however, undesirable. A3:1 mixt. of linseed-oil stand oil and tung-oil stand oil formed the best medium, varnish media being quite unsuitable. Red lead contg. 32% of PbO, gave the best results; a cortain amt. of soap formation (due to free PbO in the red lead) is desirable, but too much reaction leads to hardening of the paint in the can. Natural Fe203 contg. CaO is preferable to pure synthetic Fe O_3 , and addi. of $ZnCrO_4$ to Fe_2O_3 paints is also beneficial. A table giving the pH of aq. exts. of various pigments indicates that only those of pH greater than 7 are good anti-corrosive pigments. Paint films which absorb H₂O or are partly sol. in H₂O have little anticorrosive action. Work on the abrasion resistance, plasticity and optimum pigment/oil ratio is described, but definite conclusions have not yet been reached." From C. A.

Loon, J. van

EFFECT OF WATER ON OIL, VARNISH, AND PAINT FILMS. Verfhroniek 19, 101-2 (1946)*;C. A. 41, 604 (1947). "An improved version of the method for the detn. of the effect of water on films, given by Eibner in Ueber Fette, Oele, Leinoler Satzmittel und Oelfarben (C. A. 17, 1900), consists in applying a paint or varnish film to one side of thin, mat V₂A-steel plates. After the films are dried, the plates are immersed in distd. water of a definite temp. and taken out. The superfluous water is wiped off, and the absorbed water detd. by weighing on accurate scales with oil damping. *****The fact that constituents of the film dissolve in the water, almost proportional to time, some little (wood oil, stand oil), some very much (linseed oil to 30%), must be taken into account in the detn. of the absorption of water.********" From C. A. (abridged)

Louisville Paint & Varnish Production Club

OITICICA AS A VARNISH OIL

Paint, Oil Chem. Rev. 97 (23), 74, 76 (1935); Oil, Paint Drug. Roptr. 128(22) 54-5 (1935); C. A. 30, 4699-4700 (1936)

"Orticica and orticica-tung oil (60-40, 40-60 and 75-25) varnishes were compared with straight tung oil and tung oillinseed oil (60-40) varnishes. All the oils and oil mixts. were studied at 20- and 40-gal. oil lengths. The 20-gal. varnishes were made with wood-rosin ester gum of acid value 6-7 and an orticica oil heat-bodied for 1 hr. at 475°F. Ester gum having an acid value of 18 was used in the 40-gal. varnishes. The various varnishes were tested for drying, gas proofness and water resistance. Exposure tests were made at Louisville, Ky., during a hot dry summer. Other things being equal, the 40-gal. lengths were superior to the 20-gal. lengths. The gloss retention, general durability and protection were inversely proportional to the amt. of orticica oil in the formula for any given length. Orticica oil acts more like a resin than the usual varnish oil, hence its addn. to a wood-oil varnish tends to "shorten" the film and render it less plastic. The lack of plasticity of oiticica is indicated by failure of the film by longitudinal rupture on panels which warped slightly because of moisture absorption. These disadvantages, together with (1) the difficulty of handling the semisolid raw oil, (2) excessive foaming at bodying temps. and (3) excessive time required at top heat to attain a given body, militate against the use of oiticica in varnishes." From C. A.

Mc Clenahan, W. T.

PAINT SPECIFICATIONS FOR SEWAGE WORKS.

Sewage Works J. 13, 885-94*; Mich. State Coll., Eng. Expt. Sta., Bull. . 93, 18-29 (1941); C. A. 36, 1505 (1942).

"M. favors a primer contg. 1/3 pigment and 2/3 nonvolatile vehicle. The pigment contains 10% zinc chromate and the vehicle is a varnish of phenolic resin and tung oil. For outside service the primer is protected with an outside aluminum varnish, and for underwater service the primer is covered with a heavy coat of asphalt emulsion. M. prefers to specify performance tests rather than compn. Performance tests with cold water, hydrogen sulfide, ammonia, oil-moisture-soap emulsion are described." From C.A.

Maass, E., and Kempf, R.

RESULTS OF AN INVESTIGATION OF WHITE EXTERNAL PAINT COATS WITH REGARD TO WEATHERING AND RUST-REVENTIVE QUALITIES.

Korrosion u. Metallschutz 7, (12), 293-302 (1931)*, C.A. 26, 5773 (1932) "The results of an extension of the test periods of various paint coatings (C.A. 26, 1805, 2606) to 2-1/2 to 3 years are reported***. Expts. showed a mixt. of linseed oil and China wood oil to be better as a vehicle than linseed oil. Fe plates were painted with the same types of pigments directly on the metal. In this phase of the investigation various vehicle mixts. were also used. Not much difference was noted in the coatings produced by the 3 lithopones. A mixt. (A) of 3 parts stand oil prepd. from linseed oil and 1 part of stand oil prepd. from China wood oil seemed to be the best vehicle***." From C. A.

Maass, E., and Kempf, R.

COMMUNICATIONS OF THE RESULTS OF A SERIES OF INVESTIGATIONS ON THE WEATHER-RESISTANT AND CORROSION-PREVENTIVE PROPERTIES OF WHITE-PIGMENTED EXTERNAL FAINT APPLICATIONS, I. (2)

Korrosion u. Metallschutz 7, 265-75 (1931)*; C. A. 26, 2606 (1932). "A series of paints were applied to wood and subjected to weathering conditions. As previously shown, stand oil, China wood oil and mixts. of these proved to be very satisfactory. Addns. of benzine were unfavorable, but their effect could be nullified by addns. of stand oil and China wood oil mixts. Lithopone "olsparend" never behaved worse than pure pptd. substances and frequently behaved better. The behavior of Pb chromate pigments was noteworthy although they have the disadvantage of possessing a yellowish color." From C. A. Mattiello, J. J., and Parekh, H. V.

PREPARATION AND STUDY OF SYNTHETIC DRYING OILS. J. Sci. Ind. Research (India) PB, 29-35 (1949); C. A. 43, 6432 (1949)

"The fatty acids of cottonseed (I), fish liver (II), fish (III), peanut (IV), and tall (V) oils were esterfied with glycerol (VI), sorbitol (isomerized mixt.) (VII), mannitol VIII), pentaerythritol (Pentek) (IX), dipentaerythritol (X), and polypentaerythritol (AI) at 450 and 500°F. The course of the reaction was followed by acid.no. detn. Esterification of I was fastest with XI, X and IX, then VII, VI, and VIII. With X, II esterified fastest, then III, IV, and I, with V slowest. Esters of I with IX, X and XI dried best; the ester with VII was also good. Of the esters of X, those with III and V dried best, with IV slowest. Better drying was had with esters made at 500 than at 450°F. Small amts. of fatty acids from tung or oiticica oil in the esterification mixt. improved drying and bodying. I esterified with X bodied faster than linseed oil in the presence of maleic anhydride, crotonic acid, or sorbic but the products dried slower." From C. A.

Meyer, W.

HOW CAN TUNG OIL BE REPLACED CR MADE TO GO FURTHER? Farbe u. Lack 1937, 545; C. A. 32, 1121 (1938)

"Example varnish formulas illustrate the advantages of using artificial resins, especially the hard types, to improve varnishes made with oiticica perilla, heat-treated linseed oil or dehydrated castor oil." From C. A.

Mikusch, J. D. von

ALM VARNISH.

Farben, Lacke, Anstrichstoffe 3, 232-3 (1949); C. A. 43, 8701 (1949) "A new air-drying exterior enamel is described based on a 3:1:1 ratio of linseed, chinawood, and oiticica oil and an "oilsaving" synthetic resin." From C. A.

Muckenfuss, A. M., and Jones, Vernon

A STUDY OF MARINE PAINTS WITH A TUNG-OIL VEHICLE.

Paint, Oil Chem. Rev. 96 (14), 9-12 (1934); C. A. 28, 5997 (1934)
"Exposure tests are described on a large no. of ship-bottom paints in which tung oil is featured. Raw tung oil is unsuitable.
'fung oil bodied in the presence of a resin or mixed with resins gave good results." From C. A.

Muchle, Dr.

THICKENING OF COPAL VARNISHES

Farben-Ztg. 18, 1119-20 (1913).

The precipitation of 2n salts cannot be the sole cause of the thickening of ZnO paints because wood oils, low in acid nc., also stiffen. M. proposes that wood oil glycerides are coagulated after the fatty acids are neutralized. Variations in properties of varnishes containing different types of copal resins are discussed.

Mushle

THICKENING OF COPAL VARNISHES

Farben-Ztg. 18, 1944-5 (1913)

M. disagrees with the statements of Rosicki, Farb.-Ztg. 18, 1944-5 (1913) that all copal varnishes thicken by the precipitation of Pb and Zn salts. Wood oil does not saponify more readily than linseed oil nor does it have a higher absorption capacity for PbO. Coagulation of high molecular weight particles in wood oil varnishes by Pb and Zn pigments is a colloidal phenomenon caused by the removal by the pigments of certain acidic constituents of the varnish which had maintained those particles in dispersion.

Muehle

ON THE THICKENING OF WOOD OIL VARNISHES Farben-Ztg, 18, 2178 (1913)

M. criticizes Rosicki (Farben-Ztg. 40, 2178 (1913) for ignoring the work of Fahrion on isolation of the fatty acids of wood oil.

Muhlberg, Gottfried

CORROSION PROTECTION BY PAINT FILMS.

Kolloid-Beihefte 52, 277-402 (1941); C. A. 35, 7730 (1941) "The swelling characteristics of films prepd. by combining various pigments with Chinese wood oil and "Synourin Oil," a synthetic triglyceride of ricinic acid, were detd. by elec. resistance measurements and the corrosive effect upon an underlying Fe base was observed. While the water resistance of the films was very high, even addn. of pigments could not effect complete corrosion protection of the Fe.***" From C. A. (abridged)

Nagel, K. A.

EXPOSURE TESTS ON WHITE PAINTS.

Am. Paint J. 15 (2), 24-6 (1930)*; C. A. 25, 220 (1931)

"A preliminary report of paints exposed in 1930 and a summary of the condition of 17 paints exposed in various vehicles in 1929 are given. Of all the pigment combinations used, Pb carbonate gives the best appearance in raw linseed oil; but little difference is boiled oil was observed. From the standpoint of checking and chalking, boiled oils produce better films than raw oil. In general, the pigments were rated in the following order, best, lead carbonate, titanox, lithopone, zinc oxide, poorest." From C. A.

Nauroy, A.

THE WHITENING OF VARNISHES BY WATER

Peintures, pigments, vernis 15, 11-14 (1938); C. A. 32, 9527 (1938). "The best resistance to water is obtained with properly prepd. varnishes contg. liberal proportions of tung oil." From C. A. Nepoux, G., and Bourlot, L.

EVOLUTION IN THE USE OF DRYING OILS.

Congr. Tech. intern. ind. peintures et inds. assoc. 1947, 428-41 In the nistorical introduction the role played by tung oil in 4-hr. varnishes and in automobile finishes used after the first world war is described. The remainder of the paper is devoted to methods used to improve the drying characteristics of soft drying oils such as linseed, soybean, castor and rape oils.

1 1 1 E 2 S 2

Nordmann, J. O.

WOOD OIL VARNISHES. ...

Farbe u. Lack 1928, 448-9.

Paint Varnish Freduction Manager 16 (Apr., 1929) (abstract). "The addition of suitable resins to wood oil prevents premature gelation in the compounding of mixed wood oil-linseed oilstandol varnishes. For instance, 30 parts of a rosin product can be heated at 280 with 45 parts wood oil. The best thinner for wood oil varnishes is turpentine and the better varnishes contain at least part turpentine as the thinner. Co driers are the most suitable and are used in the form of solutions in turpentine." From Paint Vernish Production Mgr.

Obst, Walter

FLOOR OIIS

Allgem. Oel- u. Fett-Zfg. 24, 699-700; Chem. Zentr. 1928, 1, 2227; C. A. 23, 5599 (1929)

"Mineral oil of d. 0.870-0.885 with 10% turpentine oil is most commonly used. To this mixt. may be added 5-8% of ceresin, stearin, or refined ozocarite. Hard drying oils are made by boiling wood oils with a Mn varnish with an equal quantity of either benzine or benzene. This material is particularly valuable for calking. A mixture of linseed oil or wood oil is a valuable preserving agent for stone or cement floors." From C. A.

O'Connor, C. T. and Schuster, A. R.

 SOMA PHYSICAL ASPECTS OF DRYING-OIL RESIN SYSTEMS.
 Official Digest Federation Paint Vernish Froduction Clubs No. 182, 21-43 (1939); C. A. 33, 9015 (1939)

"An address giving the results of cooking tung oil with the following resins: rosin, 5% limed rosin, ester gum, modified phenolic resins and ester gum reinforced with various 100% phenolic resins. Data are given relating to the following properties of the products; color of the finished varnish, time of set of the film, drying time, Kauri reduction, acid no., resistance to 90 proof alc., resistance to 3% NaOH soln., resistance to boiling water, resistance to cold water, gasproofness and yellowing on exposure to sunlight." From C. A.

,

Odell, L. B. .

THE PAINT INDUSTRY IN TEXAS

Am. Paint J. 33 (36), 32-3, 36, 38, 40, 43 (1949); C. A. 43, 5603 (1949) (no abstract)

Tung oil is mentioned as one of the Texas products used in the Texas paint industry.

Pearce, W. T.

PRELIMINARY REPORT ON A STUDY OF PAINT VEHICLES. Paint Mfrs. Assoc. U. S. Circ. No. 219, 144-7 (Nov.; 1924); C. A. 19, 405 (1925)

"In the 1915 exposure tests at N. D. Agr. College, paints made with perilla, tung and menhaden oils gave as good service as similar paints made with raw linseed oil. Soy-bean oil gave somewhat poorer results, and cottonseed and corn oil were very much poorer. Alkali-refined, blown and other processed linseed oils gave results comparable to raw linseed oil. Various kinds of turpentines, pine oil and mineral spirits as volatile thinners in the paints showed no difference in their durability. The 1921 exposure tests very largely confirm the earlier results. New tests were begun this summer to study the effect of linseed oils of varying acid nos. and varying viscosities. Details of the prepn. of the panels and compns. of the paints are given." From C. A.

Parter, B. H.

SYNTHETIC-RESIN ENAMEL FINISHING

Metal Cleaning Finishing 10, 424-6 (1938)*; C. A. 33, 5685 (1939) "Stoving enamels are constituted from glycerol-phthalate mixts. with a carrier base blended from soybean and tung oils and a suitable pigment. Colored resins are usually sprayed at a pressure of 15-20 lb./sq. in. Methods of prepg., priming and finishing metal surfaces are outlined." From C. A.

Prager, 0.

THE MANUFACTURE OF PAINTS AND VARNISHES FOR RAILROAD COACHES. Chem. tech. Fabrik., No. 8, 166-7; Nc. 9, 187-8 (1919); Rev. . chim. ind. 28, 332-5 (1919); C. A. 15, 604 (1921)

"Exterior and interior paints for reilroad coaches must withstand extreme conditions of cold, heat, fumes, smoke, dust, shocks, etc. The vehicle is polymerized linseed oil, wood oil, or wood oil-congo resin varnish, possibly containing soy oil. A typical paint follows: 100 parts wood oil with 1000 parts resin are heated to 200-220°, 2 parts litharge, 1 part hydrated MnO₂, then 5 parts zinc oxide and 5 parts lime are incorporated in small portions. The temp. is raised to 240-250°, 100 parts stand. oil (previously heated) are added and the mixt. is dild. with turpentime or benzine. This vehicle is mixed with pigment in an amt. proportional to the oil absorption of the pigment. Varnishes for railroad coach use contain various resins, preferably the hard varieties, wood or linseed oil, resinates, oleates or borates of Pb, Mn, Zn or Co, and thinners." From C. A. Pupil, F.,

STUDY OF ZINC OXIDE GROUND IN OIL.

Recherches et inventions 17, 226-39 (1936)*;C. A. 31, 2025 (1937). "In paints, applied in 1929 and in 1931 to glass plates and exposed outdoors, lithopone shows poor results, Ti white and ZnO, each in a mixt. of equal parts tung oil and linseed oil, good results (glossy ZnO better than mat ZnO); white lead maintains its integrity, but with altered appearance." From C. A. (abridged)

Renner, F.

REVENTION OF TUNG OIL DEFECTS

Farbe u. Lack 1935, 5; Brit. Chem. Abstracts 1935, B, 239. "The development of the characteristic puckering or crystal effect in tung oil films when air-dried or stoved can be prevented by addition of 3-4% (calc. on wt. of oil) of Albertol 109 J to the properly prepared varnish before or after dilution." From Brit. Chem. Abstracts.

Rethwisch, F. B., Babcock, G.M., Yates, W., Allan, R. W., and Skett, Anthony. EFFECTS OF SOME RESINS AND OILS ON LEAFING-RETENTION PROPERTIES OF ALUMINUM PAINTS.

Paint, Oil Chem. Rev. 103 (12), 34-8 (1941); C. A. 35, 8320-1 (1941)

"The leafing-retention properties of Al paints prepd. with vehicles contg. natural resins and widely used drying oils were investigated. The prepn. of vehicles was standardized and the comparison of the Al paints was done by carefully worked-out methods. A critical investigation of exptl. results show that; (1) The resins showed decreasing leafing-retention properties in the order dammar, pale East India, Congo, batu; the oils in the order oiticica, china wood, linseed, dehydrated castor. (2) Vehicles of higher oil length (35 gallons) are better than vehicles of lower oil length. (3) The acidity of the resin is no criterion of its leafing-retention properties. (4) Surface tension is a minor factor. (5) The best vehicles are 35-gallon length varnishes using dammar or pale East India resins combined with china wood or oiticica oil." From C. A.

Rinse, J., Wiebols, W. H. G., and Takes, H. V. SWELLING OF OIL-VARNISH FILMS IN WATER

Ind. Eng. Chem. 30, 1043-6 (1933): CA 32, 8805 (1938)

"Absorption of H₂O was detd. during 21 days by the method of C. A. 31, 8956. Absorption depended upon (1) the resin (an oil-reactive phenol resin was best), (2) the ratio of tung oil to other oils, (3) the oil length (long-oil varnishes are more absorptive, especially with linseed oil, except when sensitive resins such as limed rosin are used) and (4) choice of drier, as already established." From C. A. Robertson, D. W.

VEHICLES EFFECTS IN PAINTS FORMULATED WITH TITANIUM PIGMENTS. Official Digest Federation Paint & Varnish Production Clubs No. 126, 200-7 (1933)*;C. A. 27, 4424 (1933).

"In the cases of chemically inert pigments, as Ti pigments, highly acid vehicles produced the polymerization and contg. metals in combination, e.g., Pb, Zn, Ca, produced the best gloss. Among oils, linseed and bodied oils produced the best color but the latter are slow to dry. In the case of resins, the glycerol-maleic acid-rosin types were the best for color. Good leveling was obtained with highly polymerized vehicles, such as those prepd. for non-penetrating properties. Good suspension is obtained with vehicles contg. metals, esp., Pb, cooked into the vehicle. Directions for prepg. several vehicles are given." From C. A.

Rogers, F. J.

THE OIL THAT KNOWS NO PEER Tung world 2 (11), 12-3, 20-2 (Mar., 1948) A review of the manufacture of paints and varnishes from tung oil.

Rohrig, H., and Nicolini, W.

COATING OF ALUMINUM AND ITS ALLOYS.

Maschinonbau. Der Betrieb 13, 293-4(1934); Chem. Zentr. 1934, II, 1523*;C. A. 29, 6779 (1935)

"Protection of Al surfaces by paints or other coatings is necessary only in special cases owing to the tenacious oxide film present. Because of the smooth surfaces of rolled and pressed objects, preliminary treatment prior to painting, etc., to increase the adhesion of the coat applied is indispensable. Mech. roughening destroys the oxide film and reduces the hardness of thin objects. Etching makes careful washing necessary. Treatment by the MBV or Eloxal process is recommended as increasing the adhesion of the coating applied and rendering the metal surface passive ***. Stand oil and wood oil should be added only sparingly to linseed-oil varnishes. Oil films are flexible but not very hard. Asphalt and tar films resist sea water, but shrivel and crack in the summer sun. This difficulty is eliminated by the addn. of Al bronze powder. Nitrolacquers, which are hard and only slightly elastic, can be sprayed on, but are dangerously flammable. Nitro oil lacquers have sufficient hardness and are pliable and highly resistant to corrosion. Baked lacquers can be used for Al alloys only at temps. under 120°. Al bronze, because of its light wt., high coverning and reflecting properties, is most suitable as a pigment. Errors in applying such coatings are briefly discussed." From C. A.

Rosicki, Dr.

THICKENING OF COPAL VARMISHES

Farben-Ztg. 18, 1944-5 (1913).

The thickening of varnishes with ZnO or lead acetate can be explained by the formation of Zn and Pb salts. The tendency toward thickening decreases with decrease in acid number of the melted resin. Wood oil reacts with metals more readily than does linseed oil. Al (CH) causes extensive coagulation because of the large size of the salt molecules formed.

Rosicki,	Dr. ON THE THICKENING OF WOOD OIL VARNISHES Farben-Ztg. 18, 2058-9 (1913). R. disagrees with Muchke regarding thickening of wood-oil varnishes by pigments. Wood oil varnishes will absorp over 6% of PbO and remain clear while 1-2% of PbO causes turbidity in linseed oil varnishes. Muchke's tests on the solubility of neutral soaps in benzine are not significant because varnishes may absorp metallic compounds in ways more complex than soap formation with single wood oil molecules.
Ruckert,	W. WOOD OIL OR WOOD-OIL STAND OIL. Farben-Ztg. 38, 995 (1933); C. A. 28, 3601-2 (1934). "The use of raw cil rather than preformed stand oil in tung-oil varnishes is recommended, particularly with the newer PhCH ₂ O type of synthetic resin, on the grounds of complete soln. of the resin, development to the full of its anti-gelling functions, and economy in fuel (avoidance of extra process). For mixed linseed-tung varnishes, the introduction of the former as stand oil is feasible. Typical processes are detailed." From C. A.
Schwarz,	R. COLOPHONY IN VARNISHES AND OIL PAINTS. Farbe u. Lack 1931, 123-4; C. A. 25, 2579 (1931) The low price and many uses of celophony make it a very important raw material. The principles of its uses in gloss oils, rubbing varnishes, tung oil spar varnishes, and ester gum are briefly outlined.
Schwarz,	R. ALUMINUM PAINT FOR EXTERIOR AND INTERIOR USE. Decorator 32 (383), 67-8 (1934)*;C. A. 29, 2001 (1935); "The properties of Al paints are discussed. Suitable media and primers for various surfaces are enumerated. Na ₂ SiO ₃ is unsatis- factory, since it reacts with Al. Stand-oil media (either pure linseed-tung mixts.) are most suitable. For plaster and porous cement, an ammoniacal casein emulsion medium may also be used." From C. A.
Schwarz,	R., and Schroder, F. INSULATING VARNISHES AND THE DRYING OF VARNISHES. Farbe u. Lack 1928, 425, 436, 451-2*; Paint Varnish Produc- tion Mgr.18 (April, 1929) (abstract); C. A. 23, 292 (1929). "The dielectric strength of black insulating varnishes is greater than that of yellow varnishes, and that of baked varnishes greater than that of air-dried varnishes which in turn is greater than that of spirit varnishes. Hard varnishes insulate better than soft oues. Linseed and chinawood oil varnishes, shellac, nitro-

ones. Linseed and chinawood oil varnishes, shellac, nitrocellulose and cellulose acetate solutions and asphalt are the common insulating varnish bases. The drying processes of these various varnishes are briefly discussed, and a series of formulas given, of which the following two are examples (1) Dipping varnish for high voltage underground lines:- Elaterit (an asphalt preparation) 3 and linseed sil varnish 2 parts at 200° for 5-6 hours to which are then added molten asphalt 3, linseed oil varnish 1 part, and turpentime as thinner. (2) 100 kg. neutral wool fat, 200 kg. asphalt, 100 kg. montan wax, 50 kg. rosin and 25 kg. thick raw wood oil are melted together. A number of formulas are given in which hitro-cellulose or acetyl cellulose serves as the base of the varnish; and the patent literature is briefly reviewed. One of the most generally used of these is so-called "Zellon" varnish of acetyl cellulose base, and containing oils or resins, tars, waxes, asphalt, paraffin, etc." From Paint Varnish Production Mgr.

Seebach, Fritz

ARTIFICIAL RESING AS RAW MATERIALS FOR VARNISH MAKING. Ferben-Chem. 10, 68-70 (1939)*; C. A. 33, 9020 (1939)

"The compatibility of phenol-CH₂O resins with oils can be improved (1) by using alkylated phenols, e.g., cresol or more suitably xylenol or still more suitably p-isopropylphenol, etc., (2) by alkylating, e.g., methylating, the phenolic OH group, (3) by reaction of the phenol-CH₂O resol with a drying oil or acidic resin, (4) by selecting the right oils, e.g., tung oil is more compatible than linseed oil." From C. A.

Serb-Serbin, P. W.

WATER ABSORPTION BY VARNISH AND LACQUER COATS AND ITS RELATION TO THEIR COMPOSITION

Malyarnoe Delo- 1931 (5/6), 62-75*;Chem. Zentr. 1932, I, 2388; C. A. 28, 349 (1934)

"Varnishes having exclusively liquid film formers or binders (linseed and wood bils) show the greatest H 0 absorption. The largest value is shown by oxidized oils (30%), 23.6% is shown by polymerized bils, and a max. of 15% by polymerized-oxidized oils. Addn. of wood oil to linseed decreases the H_O absorption. Russian and Chinese wood oils being quite different in this respect. Introduction of solid binders (resin esters) retards H₂O absorption, so that twice the time is required to reach the sam max. absorption, but otherwise improves H₂O absorption end resistance of the film. Increasing the resin ester and decreasing the oil content almost doubles the hardness of the film. Introduction of nitrocellulose and decreasing the oil content decrease the quantity of H2O absorbed, the film finally reaching a stable condition with 1.2-8% H₂O absorbed. Red other has no effect on the H,O a bsorption of varnishes having liquid binders (with the exception of polymerized oils); it decreases the adhesion about 23%. The same holds for varnishes with solid and liquid binders. Chrome orange greatly retards H_O absorption and increases the adhesion (liquid binders) about 25%. Pigmentized heavy oil from Chinese wood oil is an exception. PbCrO, improves varnishes with solid and liquid binders without increasing their adhesion." From C. A.

Serger, H.

VARNISH FOR PRESERVE CANS.

Forben-Ztg. 32, 685-6 (1927); C. A. 21, 1191 (1927)

"The correstive action of certain conserves (rhubarb, etc.) on their metal containers is eliminated, when the latter are coated with a baked varnish, consisting of Chinese wood oil and copals. Specifications and tests for the varnish and the varnish film and directions for their use are given." From C. A.

Skett, A., and Holzberger, J. H.

TRAFFIC PAINT STUDIES. 1941.

Am. Paint J. 26 (26), 51, 54, 56, 58-9 (1942)*: C. A. 36, 3973 (1942); "Conclusions regarding Batu cooked paints are: (1) they are the most durable traffic paints, (2) for all practical purposes it is more desirable to use linseed oil than tung or dehydrated castor oil, (3) wide flexibility of pigmentation is possible with Batu cooked vehicles and (4) Mg silicate and BaSO, are excellent inert extenders for use with Batu cooled vehicles. In spirit paint of Batu type, the best vehicles contain tung oil. Seventy parts of Ti-Ba pigment and 30 parts MgSi), give the most durable paints. Ibid. No. 28, 52-3, 56, 58. - For Batu spirit type paints the best vehicle appears to contain (by wt.) 75 parts Batu resin, 25 parts kettbbodied fish oil (Z 3 viscosity) and 100 parts high-solvency petroleum or coaltar solvent. Work on Manila type paints, white and vellow, is reviewed. General conclusions: Batu cooked paints are the most durable, those contg. tung oil are more durable than those contg. other oils and Batu linseed vehicles of about 10 gals, oil length give paints which compare very favorably with modified phenolic resin-tung linseed paints. All types of vehicles may be used with Batu type resin paint. The best Batu spirit type paints are nearly as durable as the Batu cooked paints. They require high-solvency naphthas or some coal-tar naphthas, and therefore, are not as available as Batu cooked paints." From C. A.

Singleton, W. F., and Johnson, W. C.

MOISTURE-RESISTANT COATINGS FOR METAL.

Ind. Eng. Chem. 41, 749-53 (1949); C. A. 43, 5606 (1949).

"The problem was to develop an improved sealing coat for metal objects which would be exposed to moisture-satd. atms. in the presence of small amts. of NH₃. Data are presented for a range of polymeric coatings, such as Butyl rubber, polyisobutylene, chlorinated rubber, cyclized rubber, vinyhidene chloride, acrylonitrile copolymers, vinyl chloride-acetate copolymers, phenolic varnish, polyamide, polyvinyl butyral, and polybutyl methacrylate. The best results were obtained with the polymeric materials when compared against the phenolic-China wood oil coating. The failure of the phenolic varnish may be attributed to the drying oil. Inert pigments offer some improvement over unpigmented films both in adhesion and permeability." From C. A. Snitter, Pascal

THE AGING OF OIL VARNISHES.

Bull. inst. pin 1933, 223-36*; C.A. 28, 1553-4 (1934)

"Results are given of an extensive investigation into the aging of oil varnishes, more particularly from the standpoint of ascertaining, if possible, if there are any practical methods permitting of detg. quickly and scientifically the quality of a given varnish. Varnishes were prepd. according to a no. of different formulas, from the following materials: Benguela copal, raw and polymerized linseed oil, polymerized tung oil, Bordeaux spirit of turpentine (90% b. 155-70°, acidity less than 0.15%), white spirit (distg. 100-90°, d₁₈ 0.781), Co drier, Albertol IIIL, Albertol 209L and rosin. Test panels were prepd. on wood (oak, beech) and metal (Al, duralumin, Zn and steel) and subjected to natural aging (exposure to the weather) and artificial aging (action of distd. H.O, natural H.O, 3.3% NaCl, 0.1%, H202, alternate immersion and emersion at 30-min, intervals in 3.3% NaCl at 55°, ultra-violet rays, 0_3 and heat (70°). The changes in, or deterioration of, the varnish films were observed by means of Dixmier's app. (Dutron and Dixmier, C. A. 24, 3121; Fr. pat. 705, 690, C. A. 26, 323), by detg. the rate of attack by elec. cond., and by means of the flexometer. In the latter instrument the test panel is gradually bent, the line at which bending is effected is observed under a magnifying glass, and the angle at which fissuring of the varnish film occurs is noted. Conclusions. - The natural gum varnishes were superior to the Albertol varnishes as regards resistance to weather. but inferior as regards resistance to chem. agents; Albertols confer greater elasticity and resistance to attack than copal and rosin. Boiled oil (linseed or tung) is the ingredient which confers most elasticity and resistance to attack. Spirit of turpentine is a decidely better solvent than white spirit. It improves resistance to weather and to chem. agents in propartion to its oil content; but the latter has autocatalyzing properties and acts as a drier, so that if present in excess it is injurious to the elasticity of the film. Cold immersion in 3.3% NaCl or alternate immersion and emersion in 3.3% NaCl at 55° is recommended for domparing the . resistance to attack of varnishes of the same type. The elec. cond. method indicates the resistance of the film and also its importmeability to salt water or to weakly acid solns. Artificial aging mothods are not satisfactory for evaluation the changes in elasticity of varnishes, because the results are not comparable to the effects of exposure to the weather. Use of the flexometer is recommended for following variations in elasticity," From C. A.

Steffes, N.

USE OF ROSIN AND TURPENTINE IN THE DOMESTIC MANUFACTURE OF PAINTS AND VARNISHES.

Rev. tech. luxembourg. 41, 92-8 (1949). C. A. 43, 5971 (1949). The manuf. of rosin (resinic acid. $C_{20}H_{30}O_2$) and turpentine (pinene $C_{10}H_{16}$) from fir trees is described and fields of application are discussed. "A varnish for outside use is made up of 75 kg. linseed oil and 15 China wood oil (mixing and boiling to 150° in 50 min.) 30 Congo copal or synthetic resin (to be added to the mixt. at 150°, continuing heating to 275° in 50 min., letting cool to 200°), 40 white spirit, 15 turpentine, 7 Mn drier and 5 Co drier (the last 4 to be added at 200°). The Mn drier is made up of 60 kg. rosin (heated to 220°), 2.5 Mn peroxide (to be added to the former at 220° and heated to 240°), 4 Pb oxide (dild. in linseed oil, added to former, and heated to 270°), 2 hydrated lime, 10 linseed oil (both added at 270°), 100 white spirit added after removal from fire, and let cool. Factory methods are described." From C. A.

Stevens, G. H.

CHINA WOOD OIL FORMULARY.

G. H. Stevens (Pub.), Newark, N. J., 1942.

This volume is a comprehensive compilation of more than 500 quantitative recipes and formulas with detailed practical directions for the manufacture of pain ts, varnishes, oils, lacquers, japans, drying compounds, etc. embracing the entire field of the technology of china wood oil. It was prepared as a limited manuscript edition and mineographed from original notes collected by the author.

Stewart, J. R.

VISCOSITY AND ITS RELATIONSHIP TO PHYSICAL FROPERTIES. 111. Paint Varnish Production Mgr. 14, 16-18, 20 (May, 1936)*; C. A. 30, 4700 (1936).

"A base varnish was prepd. from a phenolic resin and China wood oil and from this base ten varnishes were prepd. with nonvolatile contents down to 30% and contg. naphthenate-type drier. The Gardner-Holt method was employed for viscosity measurement. Other tests include drying time, film-thickness measurement, spreading rate, brushability and hardness on film. Conclusions: (1) there is a definite tendency toward the production of varnishes of lower viscosity (2) The viscosity and gas-proofing characteristics of a modified phenolic-China wood oil varnish can be studied by calcg. or measuring the area bounded by the cooking curve and a lower horizontal line arbitrarily selected at some point between 149° and 205°, it being assumed that time is plotted as the abscissa and the temp. as the ordinate. (3) The most desirable viscosity for a general utility varnish is 0.65-1.25 poises, so far as its effects upon other phys. properties are concerned. (4) Viscosity measurement on the base varnish or resin to be thinned is a very rapid and desirable method of detg. the solvent power of the thinner used. (5) Thinning a modified phenolic - China wood oil varnish from 55 to 40% does not appreciably affect the initial set or tack-free drying time, though hastening the dry-hard period. (6) The relationship of viscosity to nonvolatile content is not of a straight-line nature." From C.A.

Stock, Erich

RESIN STUDIES. XX.

Farbon-Ztg. 40, 1314 (1935); C. A. 30, 2780 (1936)
 "Further phys. and chem. properties of a black fossil resin
from Borneo (cf. C. A. 24, 4409) are reported. This resin, when
properly formulated with linseed oil, tung oil and ocher, yielding
good quality varnishes and enamels." From C. A.

Stumer

RELIABLE PROTECTIVE COATINGS FOR UNDERGROUND FROM PIPE LINES Bautenschutz 4, 38 (1933)*; Bldg. Sci. Abstracts 6, 165-6*; C. A. 28, 3252 (1934)

"The most suitable type of coating for protection during transport and storage consists of 10% ZnCrO₄ and 90% of a vehicle obtained by boiling 75% wood oil and 25% other vegetable or animal oil with 1% metal oxide drier. The oil should be free of resins and of the required viscosity when the pigment and 2 parts by vol. of benzine have been added. The pipes should also subsequently be given a priming coat of rust-preventive paint before the protective bituminous coating and impregnated wrapping are applied. As vehicle for the priming coat, varnish contg. wood oil is preferable to raw linseed oil." From C. A.

Suzuki, K.

STUDIES ON SOFTENING AND OIL RESISTANCE OF INSULATING CLOTH. II. PROPERTIES OF DRIED FILM OF MIXED VARNISH FROM TUNG AND LINSEED OILS.

Waseda Applied Chem. Soc. Bull. 19, 74 (1942); J. Am. Oil Chemists' Soc. 27, 432 (1950)

"The greater the linseed oil content above 25% in mixed varnish, the lower the quality of film formed. The film resisted oil less than either tung or linseed oil varnish because the mixed varnish turned into a film and dried too rapidly." From J. Am. Oil Chemists' Soc.

Sward, G. G.

WRINKIE FINISHES.

Natl. Paint, Varnish Lacquer Assoc. Sci. Sect. Circ. <u>518</u>, 257-70 (1936); C. A. 30, 7882 (1936)

"Wrinkle finishes are produced by using insufficiently cooked tung-oil varnishes or by varnishes cont. raw tung or oiticica oil. Thick films also cause wrinkling. Most wrinkle finishes contain a large amt. of drier. A resume' of the patents is given." From C. A. Sward, G. G., and Klund, H. S.

SOME OILS FOR OLEORESINOUS VARMISH. Natl. Paint, Varmish Lacquer Assoc. Sci. Sect. Circ. 595, 41-44 (1940); Brit. Chem. Abstracts. 1940, B, 377

"From comparative data (tabulated) of the hardness, kaurireduction val., resistance to 30% NaOH, 50% EtOH, cold and hot H₂O, and the exterior durability of ester-gum and phenolicresin varnishes containing various oils it is concluded that although soya-bean and dehydrated castor oils give rather longer drying times in such varnishes they may be used partly to replace linseed and tung oils." From Brit. Chem. Abstracts.

Symons, P. S.

PLASTICIZERS FOR NITROCELLULOSE LACQUERS.

Brit. Plastics 2, No. 22 (1931); Synthetic and Applied Finishes 1, 169-71 (1931); C. A. 25, 3182 (1931).

"The proper choice of plasticizers is discussed with consideration of the various purposes for which the lacquers are to be used. The main characteristics of the following principal plasticizers are described: diamyl phthalate, dibutyl phthalate, methyl-cyclohexanol oxalate, tricresyl phosphate, triphenyl phosphate, Sipalin ADM (methylhexalin ester of adipic acid), Sipalin MOM (methylhexalin ester of methyladipic acid), camphor, Bu stearate, castor oil, linseed oil, tung oil and rapeseed oil." From C. A.

Taggart, M. F.

A NOTED PAINT AND VARNISH SCIENTIST TELLS WHY TUNG TOPS ALL OTHER OTLS.

Tung World 1 (10); 4-5, 21 (Feb., 1947)

In the patented Thermolyzing process tung oil is heated for a very short period at 850°. Over 1,000,000 gallons of house paint have been made by treating 50-50 mixtures of tung and soybean oils according to this process. The manufacture of alkyd resins and other protective coatings are described.

Taggart, M. F.

TUNG OIL'S SUPERIORITY DESCRIBED BY EXPERT. Tung World 2 (5), 7, 21-2, 26 (Sept., 1947) A brief review of the uses and properties of tung oil.

Talen, H. W.

SOME PRACTICAL TESTS WITH ISOMERIZED OILS. Verfkroniek 23, 80-2 (1950)*; C. A. 44, 5610 (1950); J. Am. Oil Chemists'Sec. 27, 359 (1950) (abstract).

"The properties of linseed oil isomerized by a new process are compared with ordinary linseed oil and tung oil both boded and unbodied. The isomerized oil has better water resistance and lies between linseed and tung oils in drying time, chalking, and in scorch tests." From J. Am. Oil Chemists: Soc. ~

Tatimori, M.

GELATION OF TUNG OIL. XI. PREVENTION OF GELATION OF TUNG OIL VARNISHES AND SOME PROPERTIES OF INSULATING VARNISH. Farben-Ztg. <u>46</u>, 154-5 (1941); C. A. <u>35</u>, 8323 (1941). Essentially the same as: Tatimori, M. PREVENTION OF GELATION OF TUNG OIL VARNISHES AND SOME PROPERTIES OF INSULATING VARNISH, J. SOC. CHEM. IND. JAPAN 43 (9), 289-292B (1940).

Toch. M.

FISH OIL AS A PAINT VEHICLE

J. Ind. Eng. Chem. 3, 627-8 (1911)

The best drier for menhaden oil, used as a drying oil, is a tungate drier, made by boiling tung oil with a lead and manganese oxide. Fish cils and tung oils are the best oils for making coatings to resist heat and exposure to weather.

Tòch, M.

SOYA BEAN OIL FOR PAINT PURPOSES

J. Soc. Chem. Ind. 31, 572-4 (1912)

Cold drawn soya bean oil, in conjunction with 5-7% of a suitable drier (composed of Pb and Mn salts with Chinese wood oil and rosin) dries in 24 hrs. to a dry, hard coating.

Toronto Club

EFFECT OF TUNG AND FISH OILS IN OUTSIDE WHITE PAINTS Am. Paint Varnish Mfrs.' Assoc. Sci. Sect. Circ. 423, 1, (1932)*; C. A. 28, 2924 (1934)

"A preliminary account is given of exposures of straight linseed-oil paints and similar paints in which fish oil and tung oil have been incorporated." From C. A.

Toronto Club

PIGNENT SETTLING AND ITS MEASUREMENT.

Am. Paint J. 23, Convention Daily 16-17, 18-19, 21 (Oct. 27, 1938)*; C. A. 33, 412 (1939)

"A study of the effect of settling on the variation in colloidal aggregate in linseed, tung and perilla oils, as the oils are bodied through the complete range of practical use." From C. A.

1

Turkington, V. H., Shuey, R. C. & Butler, W. H.

PHENOL RESINOIDS IN OIL VARNISHES.

Ind. Eng. Chem. 22, 1177-80 (1930); C. A. 25, 423 (1931)

"Distinctly new types of phenol-condensation products have been developed which are sol. in drying oils without the use of rosin or an inactive ingredient to promote soly. They range from dark brown to practically colorless resins and are sol. in China wood oil; most of them are sol. in linseed oil. Useful properties of phenol resins are: durability, rapid drying, toughness, waterproofing, alk. resistance and acid resistance. The methods employed in testing these resinoids are outlined, the data tabulated on 8 varnishes and the results discussed." From C. A.

Turkington, V. H., Shuey, R. C., and Butler, W.H.

VISCOSITY INCREASE AND CELATION IN PHENOLIC RESIN VARNISH COOKING. Ind. Eng. Chem. 23, 791-7 (1931); C. A. 25, 4419 (1931).

"Two methods have been developed for detg. the optimum conditions of treatment of tung oil with natural and synthetic resins. These methods are presented with discussion of the two sets of data. An app. for detg. the gelation time of tung oil with different resins is shown in a diagram, and many curves and several tables are included. The conclusions drawn tend to confirm the assumption that the lower viscosity portion of the curve respresents chem. polymerization, or condensation, while the later portion of rapid rise is phys. aggregation or formation of gel dispersed in the other substs. present. It is believed that lack of gloss in long oil varnishes has been due to the necessity for cooking to a high body to obtain gas-proofness, with consequent gel formation. The short-cook phenolic resin varnishes have all the gloss common to short oil varnishes and have no great tendency to thicken with addn. of basic pigments such as ZnO." From C. A.

U., F. / Utz, Fritz/

CHINA WOOD OIL IN "FLATTING" VARAISHES

Farbon-Ztg. No. 43 (1905)*; Chem. Rev. Fett-u. Harz-Ind. 12, 194(1905)
It is difficult to make a good coach "flatting" varnish which
will stand pumicing after 12-14 hrs. and not regain its gloss.
Wood oil has been successfully substituted for part of the linseed
oil in such varnishes.

Ulrich, H.,

ESTERIFIED COPALS AND THE POSSIBILITIES OF USING THEM IN THE VARNISH INDUSTRY.

Farbo u. Lack 1935, 135-6*; C. A. 29, 3537 (1935).

"In discussing the use of esterified copals in varnishes it is pointed out that their use (alone or in combination with rosin, etc.), both permits replacement of considerable properties of China wood oil by linseed oil and also leads to products having excellent resistance to wear, water, heat and alky. and hence having wide possibilities of use." From C. A. Ulrich, H.

SPECIAL POSSIBILITIES OF UTILIZING IN OIL VARNISHES 100% PHENOL RESINS WHICH REACT WITH OIL AND CAN BE HARDENED. Farben-Chem. 6, 12-14 (1935)*: C. A. 29, 3537 (1935)

"The addn. of 'Superbeckite 1001," a condensation product of CH O and substituted phenols (cf. Ger. patent 563,876), to varnishes in which relatively large proportions of China wood oil stand-oil have been replaced by linseed oil stand-oil improves the gloss, imperviousness to gas and hardness of the film produced therefrom and also its resistance to wear, water, acid and alkalies to such an extent that such varnishes compare favorably or even surpass those made with China wood oil alone. The possibility of combining these types of phenol resins with drying or semidrying oils e. g., perilla oil, rape oil, blown linseed oil, soybean oil or fish oil is also mentioned." From C. A.

Vila, A.

CHINA WOOD OIL, AN INSULATING AND PROTECTING AGENT FOR MATERIALS USED IN AERO-NAUTIC CONSTRUCTION.

Peintures, pigments, vernis 10, 1-5 (1933)*; C. A. 27, 2589 (1933). China wood oil confers on paints and varnishes remarkable dielec. properties and superior impermeability.

Vongaz, S. (or Wongas, S.)

EFFECT OF PIGMENTS AND OILS ON THE ACID-FASTNESS OF COLORS. Masloboino Zhirovoe Delo 1930 (4-5), 38-40*; Chem. Zentr. 1930, II, 1449; C. A. 26 5219 (1932).

"American lampblack is the best pigment. The coating is not affected by 65% H₂SO₄. Lithopone (e.g., lithopone and lampblack) and zinc white are next in acid-fastness. Polymerized linseed oil is the best oil, then a mixt. of wood oil and linseed oil, and then oxidized linseed oil. Least acid-fastness is shown by crude linseed oil." From C. A.

Wagner, E.

DOMESTIC PLANT OILS IN OIL VARNISHES.

Farbe u. Lack 1940, 83*;C. A. 35, 2015 (1941)
Wood oil is included in a list of 23 domestic plant oils which
can be used in oil - varnishes.

Wagner, H. and Kesselring, J.

EMULSION VEHICLES.

Farben-Ztg. 34, 947-54 (1929)

C. A. 23, 2307 (1929)

Films containing tung oil adhere more firmly to glass than do those of linseed oil.

Walton, W. T.

. NATURAL AND SYNTHETIC OILS IN PROTECTIVE COATINGS.

Oil & Soap 17, 84-7 (1940); C. A. 34, 3932 (1940).

"The use of linseed, perilla, tung, oiticica, fish and other oils used for protective coatings are discussed; all have a place and usage in the manuf. of alkyd resins, which may be considered as combining oil and resin within the same mol. Castor oil can be converted into a drying oil by dehydrating the fat acid, <u>/causing it to approach</u> the properties of tung oil. Varnishes prepd. from castor oil dry rapidly and the films are resistant to hot and cold water and alkali solns., but the film is softer than that of tung oil. While it is not a direct substitute for tung oil the latter can be replaced with less change in the formula than is necessary with any other substitutes." From C. A.

Weatherston, G.

CONSERVATION OF WOOD OIL.

J. Oil & Colour Chemists'Assoc. 24, 191-8 (1941); C. A.35, 8323 (1941) "Owing to the present unavailability of tung oil in Great Britain it has become necessary to find suitable alternatives in varnish formulation. A series of 8 varnish formulas are given which use fused Congo copal or a modified phenolic resin as the hard-resin component, and either dehydrated castor oil, a linseed oil-modified alkyd, or a linseed oil-phenolic resin combination as the oil component." From C. A. (abridged).

Weise, Kurt

MOLD GROWTH ON LINSEED OIL PAINTS. I AND II.

Farben-Ztg. 39, 412-3, 444-5* (1934); Paint Varnish Production Mgr. 10 (6), 12, 14-16, 24-26 (1934); C. A. 28, 4251-2 (1934)

"A review of the literature is given. Conditions favorable to mold growth are 25-40°, high humidity and weak illumination. The mineral matter in the foots and break, and linoxyn are the important foods. Foreign deposits are of less importance. Growth is less on tung than on linseed oil. Most pigments are indifferent. Lamp black and some kinds of bone black promote growth, while ZnO, Schweinfurth green, vermillion and Cu compds. destroy the growth. The effective liquids are usually expensive or deleterious to the paint. Anions are as a rule ineffective." From C. A.

Werthan, S.

ZINC PIGMENTS IN RELATION TO SOUTHERN CLIMATIC CONDITIONS. Am. Paint J. 19, 7-9, 40-1 (Aug. 5, 1935); 14, 21-2 (Aug. 12, 1935)*; C. A. 29, 7100 (1935)

"A paint to be satisfactory in the South must; (1) withstand the destructive effects of the intense ultraviolet content of the sun, (2) resist the fungi-producing warm humid atm., and (3) adhere to the Southern pine siding. ZnO is the only white pigment exerting a fungicidal action toward mildew fungi. This action is due to a slow reaction occurring in the exposed surface layer of the film between the ZnO and the decompn. products of the linoxyn or acidic constituents of the air to form small quantities of sol. Zn salts. A very light kettle-bodied linseed-China wood oil combination makes a satisfactory vehicle when used on Southern pine. A high ZnO content is desirable." From C. A.

Williamson, B. F.

TUNG OIL DEVELOPMENTS OF THE YEAR.

Proc. Florida State Hort. Soc. Ann. Meeting 1933, 79-81; C. A. 28, 7559 (1934)

"The advantages of tung oil as a constituent of paints and varnishes, particularly for contact with sea water, are discussed." From C. A.

wolff, H.

WOOD OIL VARNISHES FOR CANNED GOODS. Farben-Ztg. 18. 2813 (1913)

The author considers wood oil varnishes to be non-toxic but advises against their use in food containers until they have been proven harmless by scientific tests.

wolff, H.

METHOD OF ANALYSIS OF OIL VARNISHES

Farben-Ztg. 29, 74-6 (1923)*; C. A. 18, 3730 (1924)

"A scheme of analysis of oil varnishes based on the usual methods of sapon., extn of free acids, extn. of unsapon. matter, sepn. of fatty acids from resin acids by esterification, etc., is given. Wood oil is indicated in the fatty acids by the n. or by the formation of crystals of Beta-eleostearic acid, and an approximation of the quantity present can be calcd. On treating the resin acids with 85% alc., the insol. portion represents the min. content of copal resins. Rosin in the sepd. resin acids is detected by the Lieberman-Morawski reaction, or the gelatinization of the soln. on addn. of a few drops of 25% WHACH. The kind of copal present may sometimes be indicated to experienced operators, by dissolving the alc. - insol. resin acids in Et.0, and making fractional extns. with 3% solns. of (NH4)2003, Na2003 and 1% soln. of KOH; and detg. the m.p., acid and sapon. nos. of the fractionated resin acids. Rosin oils, pitches, asphalts, etc., may be detected in the unsapon. matter by color reactions, solubilities, etc. The diazo reaction serves as a confirmatory test for coal tar pitch. If the amt. of unsapon. matter is small, the presence of copal resins is not likely; if it is appreciably greater than the amt. of resin acids, the presence of damar is probable. Methods for the detn. of the metallic driers are given." From C. A.

Wolff, H.

WATER-RESISTANT PAINTS.

Farben-Chem. 1, 20-2 (1930)*;C. A. 25, 3850 (1931).

"The water-resistance of a paint film is dependent jointly on the following 4 factors; porosity of film (direct transmission of water), tendency of film to swell (indirect transmission of water), "Solidity" of a film (true resistance to water), and adhesion. Thus by addn. of treated tung oil to a linseed oil paint, porosity and swelling tendency are diminished, but adhesion is weakened. The water-resistance (on continuous and intermittent immersion) of 2-coat systems comprising white lead paint, alone and with the addn. of 10 and 20% of a proprietary paraffin dispersion, "Enkaustin," all the possible rearrangements of these as undercoats being-used, was detd. The system white lead undercoat-white Pb + 10% of "Enkaustin" finishing coat was the most resistant. It is pointed out that the water-resistance of the undercoat must not be raised to the point where adhesion suffers, and that a protective action on the undercoat should be exercised by a water-resistant finishing coat." From C. A.

Wolff, H.

COMBINATIONS OF NITROCELLULOSE WITH OILS Paint Varnish Production Mgr. 9 (3) 22-3, 30-4 (1933); C. A. 27, 2048 (1933)

11. Bat

"Low-viscosity cotton gave films in all proportions with untreated linseed oil. In the case of bodied oils, both linseed and tung, the higher the percentage of oil, the clearer the films. Oil in combination films oxidizes more slowly than that in films contg. oil only, but this oxidation has very little influence on the mech. properties of the films (cf. C. A. 25, 5779). The influence of solvents and plasticizers is minor and usually adverse. Combination films consist of 2 phases with different oil-nitrocellulose ratios. The continuous phase of clear films is the richer in oil." From C. A.

Wullen-Scholten, W. van

EXPERIMENTS WITH FUME (SMOKE-PROOF) PAINTS.

Farben-Ztg. 36, 1690-1 (1931)* C. A. 25, 4721 (1931).
 "Red lead primers and tung oil stand oil top coats are not
suitable for exposure to combustion fumes. Whether the red lead
was fresh or aged, subsequent coats of tung oil stand oil
blistered." From C. A.

Zhebrovskii, V. V., Ioganson, G. Ya., and Kazanskaya, M. I. THE EFFECT OF SMALL ADDITIONS OF WOOD OIL ON SOME PROPERTIES OF FILMS OF INSULATING LACQUERS.

Lakokrasochnuyu Ind. Za 1935 (2),16-19*; C. A. 29, 67.77 (1935); "The addn. of wood oil has almost no effect on insulating ability. Lacquers prepd. by the cold process are somewhat better insulators than those prepd. hot." From C. A.

Zilberman G., and Bolotin, A.

SYNTHESIS OF LACQUERS

Lakokrasochnuyu Ind. Za 1933 (2), 27-30*; C. A. 27, 4696 (1933)

"Expts. showed that in the interaction of colophony.rosin and fatty acids, under conditions approximating lacquering in practice, definite chem. reactions take place. Based on these reactions a no. of condensations of colophony rosin with fatty acids of wood cil, rapeseed oil and castor oil were conducted." From C. A.

Zinov'ev, A. A. (or Sinowjew, A. A.)

THE USE OF OXIDIZED OILS IN THE PRODUCTION OF OIL VARNISHES. Malyarnoc Delo 1932 (4), 15-18*; Chem. Zentr. 1932, II, 2740; C. A. 27, 5993 (1933);

"A discussion of the role of China wood oil and the possibility of its replacement by oxidized linseed oil in the manuf. of the more expensive oil varnishes." From C. A. (i) Miscellaneous Uses

Gutkin, S. S.

MISCELLANEOUS USES OF DRYING OILS.

J. Am. Oil Chemists' Soc. 27, 538-44 (1950).

Tung or Chine wood oil is used for core oils which bind send to form molds in which metal castings are made, brake linings, wood impregnants and insulating varnishes.

Hall, J. G.

THE ROLE OF SYNTHEIIC RESINS IN THE MANUFACTURE OF PRINTING INKS. I. , Oil& Colour Trade J. 93, 579-80 (1938); C. A. 32, 3641 (1938). "A discussion of the relation between consistency properties of the vehicle and ink and the new synthetics. Consistency properties are flow, length and tack. Length regulates the distribution of ink between the printing and the printed surfaces and the leveling properties of inks when spread on printed and printing surfaces. Tack regulates the transfer of ink from the printing to the printed surface owing to the adhesion to the 2 surfaces and can be measured by various adhesion test methods. These 3 properties are interrelated. Resin groups have proved useful in the modification of printing characteristics of ink vehicles. Ester gums add tack -the more the higher their acid values; esterified copals increase tack without reducing length. Maleic acid resins are more viscous than ester gums and impart length and increase tack. Phenolic resins do not increase length of the vehicle according to their own degree of polymerization. Phthalic resins impart length and tackiness. Phenol cured tung oil, produced by dispersing 1 part resin in 2-1/2 parts tung oil, heating the mixt. to 175° to 200° in 30 min. and chilling back immediately adds to the vehicle length without tackiness. Chem. reactivity of basic pigments in inks leads to soap length and reduction of tack, and may result in the formation of a plastic rubbery mass or a solid gel. These results may be avoided by satisfying the chem. activities of the pigment with org. acids. The acids form a soap envelope around the pigment perticles. Gelation is liable to occur if phthalic resins of low oil content, which have been over-polymerized in the varnish kettle, or phenol-cured tung oil excessively boiled are added." From C.A.

Krauss, V. P.

COBALT DRIERS.

Eighth Intern. Congr. Appl. Chem. Section: Paints, drying oils and varnishes, 8, 127-131 (Sept., 1912); Chem. News, 107, 188. (Apr. 18, 1913).

The tungate of cobalt is prepared by saponifying tung oil with NaOH and then precipitating with a salt of Co. It must be washed, dried and fused with great care since it oxidizes readily becoming useless. It may be fused with resinate to form a resino-tungate. For use, 0.5-5.0% is incorporated into oils at 300-500°F. Lavers, C. G.

PACKAGING. VII. WATERPROOFING OF FIBERBOARD CONTAINERS.

Can. J. Research 25F, 128-32 (1947); C. A. <u>41</u>, 4645 (1947). "An attempt was made to find a material in which domestic fiberboard cartons could be dipped to produce waterproof packages. The waterproofing agents tested included vinyl resins, cellulose acetates, nitrocelluloses, polystyrene, chlorinated rubber, corn-protein resin, a wood oil drier combination, an alkyd and a microcrystalline wax." From C. A. (abridged)

Lundberg, A. H.

HARDBOARD AND ITS MANUFACTURE.

Pulp & Paper 22 (12), 82,84,93 (Nov., 1948).

Technical and economic factors of defibering, pressing, treating and marketing are broadly discussed. Tempered hardboard is produced by adding emulsified tung or linseed oil or phenolic resins to the pulp (or by imprognating a pressed sheet) and then heat treating the board in hot-air chambers.

O'Hare, G. A.

DRYING OILS IN THE FLOOR COVERING INDUSTRY.

J. Am. Oil Chemists' Soc. 27, 530-3 (1950).

The use of drying oils in the manufacture of printed felt base and of linoleum is reviewed. The hard oils, such as tung, oiticica and dehydrated castor oil, are frequently used in combination with softer oils (linseed, soybean, etc.) in making the "print paint" of printed felt base floor coverings. The hard oils are generally unsuitable for use in linoleum because their oxidation products have poor binding properties and low tensile strength. The 1948 consumption of drying oils for floor coverings is listed as follows (in millions of pounds): linseed, 110; soybean, 22; Chinawood, 9; fish, 5; dehydrated castor, 0.7; oiticica 0.16; others, 0.13.

Pagani, Dante

DRYING CATALYSTS FOR LINSEED OIL.

Congr. tech. intern. ind. peintures inds. assoc. 1, 369-74 (1947) (in Italian); C. A. 43, 8699 (1949).

"Resinates, linoleates, and naphthenates of Pb (23.43, 24.65, and 29.88% Pb), Mn (6.86, 8.64, and 10.96% Mn), and Co (6.96, 9.12, and 12.25% Co) were prepd. by the pptn. method, and their wt. loses on heating for 24 hrs. to 110, 150, and 200° detd. The loss was highest with Co resinate (6.15, 10.70, '16.00%), while the other materials differed less and their order of loss varied with the temp. The drying action of the Mn salts of the fat acids of oiticica oil, chinawood oil, perilla oil, and grapeseed oil on linseed oil (I) fell in the order given (0.6% Mn optimum)." From C. A. Suen, T. J., and Yao, F. H.

SOME CHINESE CLAYS AS ADSORBING AGENTS.

J. Inst. Petroleum <u>31</u>, 179-87 (1945); C.A. <u>39</u>, 5073 (1945). "Two clays of Nanchuan, one of them classified as collyrite, the other as cimolite, and a Tsunyi halloysite sample were tested as to their ability to reduce the gum content of gasoline made by cracking tung oil. The collyrite was treated with H₂SO₄ and with HCl, and the addn. of Fe, Al, and Mg salts was also tried as a means of increasing the adsorptive power. Gasolines, rapeseed oils, and lubricating oils required different temps. for the best results in decolorization. Acid treatment and the addn. of salts scarcely improved the action of the collyrite. Only the halloysite showed sufficient gum-reducing power to be useful commercially." From C.A.

Tchang, H. L. and Wang, Y. C.

STUDY ON THE PREPARATION OF DRYING OILS FOR OILED CLOTH AND OILED SILK.

Contrib. Inst. Chem., Natl. Acad. Peiping 2, 57-72 (1936)*; C.A. <u>31</u>, 4142 (1937).

"The oil film formed after drying is always stiff and nonsticky, irrespective of the temp. and time of drying or of the nature and amt. of driers, if boiled oil consists of tung oil only. A mixt. of driers is always more active than an equal wt. of any of its constituents. The quantities of driers required for hastening the drying of tung oil and imparting transparency to silk or glassy surface to cotton cloths vary considerably with the nature of the driers. Mixts. of tung oil with other oils generally require less drier than tung oil alone for boiling to impart the same degree of transparency to silk. Oiled cloths made from linseed oil or bean oil dry more slowly than tung-oil products and remain sticky after drying. Oiled products made from tung oil are nonsticky, but stiff." From C. A.

Toeldte, W.

WOOD PORES AND PORE FILLERS.

Farbe u. Lack 1931, 316-8; C. A. 25, 4722 (1931).

"A commercial, cil-free wood filler was applied in 1-coat work to thin panels of several kinds of wood and the depth of penetration observed microscopically. Coarse wood such as oak showed less penetration than fine-grained wood such as beech. The permeability of addnl. panels to air before and after coating with 5 different types of fillers was detd. (cf. C.A. 24, 2900; 25, 608). The results were erratic, but, in general, fillers composed of bodied tung oil, of a mixt. of a tung-oil rubbing varnish and boiled linseed oil, a commercial oil-free filler and a commercial filler of unstated type reduced the permeability of the coated panels to 1/6, while boiled linseed oil reduced it to only 1/3 of that of the uncoated panels." From C. A. Waele, A. de

MANUFACTURE OF LINOLEUM AND ITS VALUATION.

Ind. Eng. Chem. 9, 6-18 (1917); J. Soc. Chem. Ind. <u>36</u>, 149-50 (1917) (abstract)

Linoleum is discussed under the following headings: (1) manufacture, (2) reactions, (3) action of solvents on oxidized oils, (4) linoxyn and cyclolin, and (5) resins and Chinese wood oil in cements. Although the use of Chinese wood oil has been patented as a substitute for kauri gum it has no chemical influence on the transformation of the oils and is disadvantageous as it reduces the amount of oxidized oil that may be used in the mixture.

Wang, C. C.

TUNG-OIL SOAPS AS DRYING AGENTS WITH TUNG OIL, AND TRANSPARENCY OF THE PRODUCT.

Science (China) 17, 881-92 (1933)*; C.A. 27, 5992 (1933).

"Mn soap is an excellent drier and is superior to other metallic tung-oil soaps. In the prepn. of tung oil for use, if it is mixed with 1/4 its wt. of resin and heated to 250° (not higher) for 10-15 min. and then heated longer at lower temp., the product maintains its transparency." From C. A.

Wise, L. E., and Duncan, R. A.

DRYING PROPERTIES OF LINSEED OIL TREATED WITH COBALT LEAD AND MANGANESE ELAEOSTEARATES.

Ind. Eng. Chem. 7, 202-5 (1915); C. A. 2, 970 (1915).

The procedures for the preparation of the soaps are given. The Pb soap was a white powder, the Mn soap a nearly white powder while the Co soap was a pink curd which dried to a rich purple. Each accelerated the drying of linseed oils.

Wright, W. H., Bozicevich, J., and Underwood, P. C. CRITICAL TESTS OF MISCELLANEOUS DRUGS AS ANTHELMINTICS FOR ASCARIDS, WHIP-WORMS AND NODULAR WORMS OF SWINE. North Am. Voterinarian 12 (b), 27-35 (1931)*; Expt. Sta. Record 65, 874 (1931) (abstract)*; C. A. 26, 3839 (1943). "The details of tests made of hexylresorcinol, tung oil without

"The details of tests made of hexylresorcinol, tung oil without a purgative, 2-chlorpentane, tetrachloroethylene in hard gelatin capsules and butyl chloride as anthelmintics are reported in tabular form." From C. A.

1

V. ELEOSTEARIC ACID AND ITS DERIVATIVES

Alpar, S. R.

THE DRYING OF MAHALEB OIL AND MAHALEB STAND OIL.

Rev. faculté sci. univ. Istanbul A14, 111 (1949)*; C.A. 44, 6655-6 (1950); J. Am. Oil Chemists' Soc. 27, 432 (1950).

"Mahaleb oil from <u>Prunus mahaleb</u> had average analytical values of: acid value 2.5; sap. value 189; and iodine number 153. The component acids were eleostearic 36%, linoleic 41%, and oleic 33%. A stand oil prepared by heating the oil to 300° for 2.5 hours had and iodine number of 108. The unbodied oil air dried in eight days while the stand oil air dried in 35 days." From J. Am. Oil Chemists' Soc.

Alper, S. R., and Esin, S.

FATTY ACIDS OF MAHALEB OIL.

Rev. faculté sci. univ. Istanbul <u>A13</u>, 199-204 (1948); C.A. <u>43</u>, 2791 (1949).

The solid fatty acid present to the extent of 36% in mahaleb oil was identified as a-eleostearic acid; this accounts for the drying properties of the oil.

Andes, L. E.

OIL VARNISH TREE OIL, CHINESE WOOD OIL, TUNG OIL. Vegetabilische Fette und Oele, A. Harteben's Verlag, Wien, Pest, Leipzig, *1896, p. 203-4. An English translation of this selection is found in Patents, Technology, and Bibliography of China Wood Oil (Tung Oil) 1914, Vol. 2, Part 1, pp. 2009-10.

The oil is said to be from the seeds of elaeocca, syn. <u>Aleurites</u> <u>cordata</u>, indigenous to China and Japan. Cloez has stated that this oil is composed of oleine and a glyceride called elaeomargarine, which on saponification gives elaeomargaric acid (margarolic acid) $C_{16}H_{30}O_3$. The author considers the latter improbable on account of the formula and considers it likewise improbable that the oil is first transformed in the air into a fat which melts at 32°C.

Ault, W.C., Cowan, J.C., Kass, J.P., and Jackson, J.E.

POLYMERIZATION OF DRYING OILS -- COMPARATIVE RATES OF POLYMERIZATION OF ESTERS OF ISOMERIC OCTADECATRIENOIC ACIDS AT 275° IN VACUUM. Ind. Eng. Chem. 34, 1120-3 (1942); C.A. <u>36</u>, 6360 (1942).

"The rates of thermal polymerization at 275° of the various conjugated trienoic esters investigated have the same order of magnitude, although methyl pseudo eleostearate polymerizes slightly faster than its positional isomers, methyl a- and methyl β -eleostearate. These rates are much more rapid than those of the 2 unconjugated trienoic fatty acid esters examd. The fact that the geometrically isomeric forms of the trienoic acid esters have approx. the same rates of thermal polymerization, but at the same time have widely different oxidation rates, may account for the anomolous behavior of certain oils in which no previously predictable correlation has been found between speed of gelation and rate of drying. Addnl. evidence in conformity with Scheiber's theory of isomerization (C. A. 24, 978) and the Kappelmeier theory (C. A. 27, 4425) of diene mechanism of polymerization of unsatd. fat acids or their esters has been presented. By a simplified interpretation of 1,4-diene addn. of conjugated trienoic acids, structures for a bicyclic trimer and a tricyclic dimer have been suggested to account for the phys. properties of the polymerized products." From C. A.

Bauer, K. H.

CHINESE WOOD OIL. II. ELEOSTEARIC ACID.

Chem. Umschau Fette, Oele, Wachse u. Harze <u>33</u>, 53-6 (1926); C.A. <u>20</u>, 3583 (1926).

"Pure c-eleostearic acid was heated to 200° in an atm. of CO2 and the escaping vapors were absorbed in H2SO4. The pure acid had acid no. 200.4, sapon. no. 200.4 and I no. 181.2. After heating, the acid no. fell to 152.4, the sapon. no. increased to 206.3, while the I no. fell to 88.7 in one expt., and to 176, 213.8 and 85.4, resp., in another; the total loss by vaporization was 10.6% after 19 hrs. in the first expt. and 13.8 after 36 hrs. in the second expt. Pure 8eleostearic acid was similarly heated in CO2, the product showing an acid no. of 145.1, sapon. no. of 235.8, and an I no. of 79.1 in one case, and 163.6, 247.6 and 92.6, resp., in another. These results indicate anhydride formation since acid no. and sapon. no. do not go parallel. The vapors absorbed by H2SO, were extd. with ether and the united product of 4 expts. showed an I no. of 14.9 and 15.2; apparently a cracking of the eleostearic acid had occurred with formation of H₂O and unsatd. compds. The increased sapon. no. of the heated acids suggests splitting into compds. of smaller mol. wt.; the mol. wt. of the polymerized β acid in C₆H₆ soln. was 4633 and 4588.2 by the Rast camphor method 2285.6; the mol. wt. of the polymerized a-acid in C6H6 soln. was 985.6 and by the Rast comphor method 490.9. Attempts to sep. the polymerized products into a sol. and an insol. portion by means of solvents, or into a free acid and sapon. compds. by means of K2CO3, were unsuccessful. Hydrogenation of the polymerized a-acid in alc. soln. at room temp. and 45 lb. pressure yielded mainly stearic acid." From C. A.

Bauer, K. H.

POLYMERIZATION AND OXIDATION OF UNSATURATED FATTY ACIDS. Chem. Unschau Fette, Oele, Wachse u. Harze 33, 198-9 (1926); C.A. 21, 2809 (1927).

"a- and β -eleosteeric acids were heated in CO₂ to 200°, producing a thick polymerized oil and some volatile acids, hydrocarbons and H₂O. The polymerized oil has a lower acid no. but a higher sapon. no. than the original, and an I no. between 70 and 90, against the original 181.2. Anhydrides and estolides have apparently formed and possibly some non-volatile acids of lower mol. wt. The product of the a-acid showed a mol. wt. of 4588 in C₆H₆ and 2285 by Rast's Camphor method, while the β -acid showed 985.6 in C₆H₆ and 490 in camphor. On hydrogenation at 4 atm. the polymerized a-acid yielded stearic acid and a little β -eleostearic anhydride, while the β -acid absorbed H₂ readily but remained a thick oil; mol. wt. before hydrogenation 4588 and after hydrogenation 1030 in C₆H₆ and 2285 and 525, resp., in camphor." From C. A. (abridged) Benedikt, [R.]

ELAEOMARGARIC ACID.

In Lewkowitsch, J. Chemical Analysis of Oils, Fats, Waxes, and of the Commercial Products Derived Therefrom. From the German of R. Benedikt. Rev. and enl. Macmillan and Co., London and New York, 1895, p. 23.

Elaeomargaric Acid, C₁₇H₃O₂, occurs as the glyceride in the oil of Elaeococca Vernicia. The ²acid, m.p. 48° C. crystallizes as rhombic plates and readily absorbs oxygen. On exposure to light in alcoholic solution, it changes to its isomer, elaeosteric acid, m.p. 71° C.

Boeseken, J.

COMPOSITION OF ALPHA-ELEOSTEARIC ACID, THE MOST IMPORTANT COMPONENT OF CHINESE WOOD OIL (TUNG OIL).

J. Soc. Chem. Ind. 48, 71-2T (1929); C. A. 23, 5160 (1929).

"Criticism of the paper by Steger and van Loon C. A. 23, 5050." From C. A.

Boeseken, J., and Ravenswaay, H. J.

THE INDEX OF REFRACTION OF CHINA WOOD OIL AND THE COMPOSITION OF ALPHA- AND BETA-ELEOSTEARIC ACIDS.

Rec. Trav. Chim. 44, 241-3 (1925); C. A. 19, 2475 (1925).

"China wood oil (I), is about 90% glyceride of α -eleostearic (or α -eleomargaric) acid (II) considered to be an isomer of linolic acid because its I no. (160-70) indicates 2 double bonds. II, m. 47°, can be converted into the β -isomer (III) m. 67°. I irradiated with a Hg lamp is converted in 48 hrs. into a solid mass of the glyceride of III, m. 58.5°. The mol. refraction of purified I is 284.6 (calcd. 267.6); for III it is 289.9 (calcd. 267). On the basis of these data and a comparison with unsatd. hydrocarbons B. and R. conclude that I and III are probably isomeric compds. with 3 double bonds. The mol. refraction of pure II is 93.05 (calcd. 86.04); of linolic acid 86.57 (calcd. 86.04). I hydrogenated in the presence of Ni absorbed 7.9 mols. Ho (calcd. 9.0). The results indicate that there are more than 2 double bonds but B. and R. are unable to state why the calcd. amt. of H₂ was not absorbed. II is therefore not a linolic acid but is \tilde{a} linoleic acid and both the α - and β -forms have the compd. Me(CH₂)₂CH:CHCH : CHCH:CH(CH₂)₂CO₂H. This result seems to disagree with the I no. but it is pointed out that compds. with 3 conjugated bonds unite easily with only 2 mols. of Br2." From C. A.

Boeseken, J., and Ravenswaay, H. J.

THE COMPOSITION OF ALPHA-ELEOSTEARIC ACID OF CHINESE WOOD OIL AND ITS ISOMER BETA-ELEOSTEARIC ACID. Verslag Akad. Wetenschappen Amsterdam 34, 204-7 (1925); C. A. 19,

2475 (1925).

"The very high mol. refractions of α - and β -eleostearic acids and their derivs., which exceeds by 5-7 that calcd. with the aid of the generally accepted formula, suggested the existence of 3 conjugated double bonds. The absorption of 2.65 mols. H by wood oil and Et α -eleostearate on hydrogenation with H and Ni catalyst confirmed this hypothesis. The formula suggested by B., Me(CH2)3 CH: CHCH: CHCH: CH(CH2)7CO2H, is in keeping with the high drying

power and the formation of large quantities of azèlaic and valeric acids by ozonization, but does not explain the formation of succinic acid. The low I value, corresponding to 2 double bonds only may be attributed to the abnormal behavior of compds. with 3 conjugated double bonds as was recently stated by Mueller." From C. A.

Boeseken, J., and Ravenswaay, H. J. CONSTITUTION OF ALPHA-ELEOSTEARIC ACID FROM CHINESE WOOD OIL AND ITS ISOMER BETA-ELEOSTEARIC ACID.

Proc. Acad. Sci. Amsterdam 28, 386-9 (1925); C. A. 20, 44 (1926).
Essentially the same as Böeseken & Ravenswaay "The Composition of α-eleostearic acid of Chinese Wood Oil and Its Isomer β-eleostearic acid" (Verslag. Akad. Wetenschappen Amsterdam 34, 204-7 (1925)).

Bradley, T. F., and Johnston, W. B.

DRYING OILS AND RESINS. REACTIONS INVOLVING THE CARBON-TO-CARBON UNSATURATION DURING THE THERMAL TREATMENT OF SOME ESTERS OF UNSATURATED $\rm C_{1B}$ FAT ACIDS.

Ind. Eng. Chem. 32, 802-9 (1940).

"The Me esters of the acids of olive, dehydroxylated castor, soybean, linseed, and tung oils were polymerized at 300° and the products sepd. by distillation. By means of T. no., sapon. no., mol. wt., density, etc., it was shown that the products were principally dimers and were of bicyclic structure in the case of trienes (tung oil) and monocyclic in the case of dienes (linseed oil, etc.). There were also formed esters of lower mol. wt. than the monomer (by splitting of the hydrocarbon chain) and of mol. wt. between monomer and dimer (by addn. to the monomer of the hydrocarbon fragment of the above split)." From C. A.

Bradley, T. F., and Richardson, D.

DRYING OILS AND RESINS. ULTRAVIOLET ABSORPTION STUDY OF ESTERS OF THE ACIDS OF DRYING OILS.

Ind. Eng. Chem. 32, 963-9 (1940); C. A. 34, 6104 (1940).

"Ultraviolet absorption methods are useful in the study of polymerization of drying oils to indicate the presence of conjugated double bonds and in some cases cyclic or aromatic molecules can be detected. Distn. of heat-polymerized Me esters of the acids from a drying oil yields residues which absorb ultraviolet light more strongly than monomeric distillates. Data on changes in the absorption spectra of linseed and tung oils upon heat-bodying indicate that considerable amts. of unreacted acids are still present in these oils as the gel point is approached. In the case of linseed oil, there is a net increase in the amt. of conjugated acids present in the first stages of heat-treatment, followed by a gradual decrease." Fron C. A.

Brauer, R., and Steadman, L. T.

THE AUTOXIDATION OF BETA-ELEOSTEARIC ACID. THE APPLICATION OF THE SPECTROPHOTOMETER TO THE STUDY OF THE COURSE AND THE KINETICS OF THE REACTION.

J. Am. Chem. Soc: <u>66</u>, 563-9 (1944); C. A. <u>38</u>, 2553 (1944). "A method is described for the study of the autoxidation of fatty

"A method is described for the study of the autoxidation of fatty acids in liquid soln. by O-uptake measurements and by the simultaneous

- 351 -

detn. of the absorption spectra of the autoxidizing solns. Curves showing the relation between the rate of O-uptake of β -eleostearic acid and the initial concn. of the substrate are presented. From the spectrographic changes observed in autoxidizing solns. of β eleostearic acid, it is suggested that during the reaction a conjugated diene is formed which in turn undergoes autoxidation. A method is described that permits employing (a) the O-uptake curves and (b) the relation between absorbed 0 and residual intact triene groups. It is assumed (a) that the initial uptake of 0 by β eleostearic acid results in a dimerization involving the formation of some C-C bonds and (b) that a parasitic polymerization reaction is induced by the peroxides formed in the course of the reaction. The formation of dimeric products in the reaction was verified by mol.-wt. detns. The amount of O taken up can be computed approx. for the early stages of the reaction from the extinction coeffs. of the diene and the triene bands if the following sequence of reactions is assumed: $2(--C=-)_3 + 0_3 - (--C=-)_2$. $(-C==C-)_2 + 0_2 \rightarrow$ spectrographically inert products capable of taking up $\tilde{2}$ mols. of 0 per mol. of original β -eleostearic acid. The rate of O absorption by β -eleostearic acid becomes insignificant after an uptake of 2 mols. of 0 per mol. of β -eleostearic acid." From C. A.

Brod, J. S., France, W. G., and Evans, W. L.

THERMAL POLYMERIZATION OF ETHYL ELEOSTEARATE AND 9,11- AND 9,12-ETHYL LINOLEATE.

Ind. Eng. Chem. <u>31</u>, 114-18 (1939); C. A. <u>33</u>, 2105 (1939).

"Et α -eleostearate (I) and a mixt. of Et 9,11- (II) and 9,12linoleate (III) (obtained through the dehydration of ricinoleic acid and contg. 30-50% of II) were heated in sealed, evacuated tubes at 300° for periods up to 20 hrs. Mol. wts., I nos., and diene nos. were detd. I reached an equil. in 1 hr. and II + III in 5 hrs., forming about 75% of polymer in each case. The rest was a monomer distg. in high vacuum. The polymers showed no particles of colloidal dimensions in the ultramicroscope and are dimers, in which the 2 chains are probably united through a common 6-membered ring. The monomer distd. from polymerized I appears to be a cyclic isomer but not the 5-butyl-1, 3-cyclohexadiene-6-caprylic acid suggested by Rossman (C. A. 27, 5057), since the product had no diene no. The mixt. of II + III gave apparently the same product as III alone (cf. C. A. 30, 890). The residual monomer was II. Thus III appears to isomerize to II rather than polymerizing directly." From C. A.

Brown, W. B., and Farmer, E. H.

UNSATURATED ACIDS OF NATURAL OILS. III. THE HIGHLY UNSATURATED ACID OF THE KERNELS OF PARINARIUM MACROPHYLLUM.

J. Chem. Soc. 1935, 761-3; C. A. 29, 6085 (1935).

"The highly unsated. acid from the oil of Parinarium macrophyllum (cf. Steger and van Loon, C. A. 28, 2929), which m. 45.5-6.5°, is shown to be α -eleostearic acid." From C. A.

Chen, M. C., and Hu, D. B. (with, in part, Wong, P. H.)

OXIDATION OF NATURAL FATS AND OILS. II. KINETICS OF OXIDATION OF ALPHA-ELAEOSTEARIC ACID WITH SODIUM DICHROMATE CATALYSED BY TRICHLOROACETIC ACID.

J. Chinese Chem. Soc. <u>10</u>, 173-179 (1943)*; Brit. Chem. Abstracts <u>1944</u>, B, II, 205.

"Kinetics of oxidation of α -eleostearic acid (I) (tung oil contains ~ 80%) by aq. Na₂Cr₂O₇-AcOH at 25° in presence of 1% or 3% of CCl₃.CO₂H show that stage I of the oxidation is rapid, being ~60 times as fast as Stage II, and both stages are bimol. It is assumed that stage I ends (5-10 min.) before stage II begins; stage I is accelerated by 3% of CCl₃.CO₂H. A mechanism is postulated in which the intermediate products are the (OH)₆- and the triperoxidederivative of (I)." From Brit. Chem. Abstracts.

Cloez, S. . .

THE OIL OF ELAECCOCCA AND ITS SOLID MODIFICATION PRODUCED BY THE ACTION OF LIGHT.

Compt. rend., <u>82</u>, 501-4 (1876)*; Chem. News <u>33</u>, 129 (1876); Bull. soc. chim. <u>28</u>, 23-4 (1877)*; J. Chem. Soc. <u>30</u>, 102 (1876).

Alcoholic KOH (50%) saponifies the oil and acidification with dil. H₃PO₄ gives glycerine, a solid acid, which C. named margolic, and a liquid one which he named elaeolic acid. The latter has been obtained in pure form by treating the mixed acids with chalk, extracting the Ca scap of the liquid acid with ether and decomposing it with HCl. K, Ba, Pb and Ag Salts of margolic acid were studied as well as an acid K salt. The K salt is readily purified by recrystallization from ethanol. Margolic acid crystallized in rhomboidal plates, melts at 48°C., is soluble in ether, CS₂, liquid hydrocarbons and alcohol, readily takes 8.5% its weight of O₂ from the air. It is composed of C, 71.5%; H, 10.94; and 0 (by diff.), 17.56% or the formula ($C_{24}H_{20}O_{6}$). Elaeolic acid forms a Pb salt soluble in ether. Saponification of oil solidified by exposure to light yields an acid (C, 74.30%; H, 11.10%; O, 14.54%) which C. names stearolic. It melts at 72° but contains less oxygen than does margolic acid.

Cloez, S.

THE MODIFICATIONS OF ELAEOMARGARIC ACID, OBTAINED BY THE ACTION OF LIGHT AND HEAT.

Compt. rend., <u>83</u>, 943-5 (1877)*; Bull.soc. chim. <u>28</u>, 23-4 (1877)*; J. Chem. Soc. <u>31</u>, 454 (1877).

"The oil obtained from the seed of Elocococca vernicia, when saponified with an alcoholic solution of potash, yields a well crystallised salt, from which may be separated a solid fatty acid melting at 43°. This is elaeomargaric acid. Solutions of this substance in ether or carbon disulphide remain unchanged for an indefinite time when kept in the dark; but when they are exposed to light, the acid is modified, so that when the solvent is removed by distillation in a current of hydrogen, the residue melts at 71°. An alcoholic solution of the acid when exposed to light deposits fine crystals, which have the same composition as the original acid. This modification the author terms eloeostearic acid.

When heated to 180° in sealed tubes containing hydrogen, these acids are changed into a liquid product having the same composition, but upon which light is without action. This modification receives the name of elaeoleic acid." From J. Chem. Soc.

Dingwall, A., and Thomson, J.C.

SPECTROSCOPIC STUDY OF ELEOSTEARIC ACIDS FROM CHINESE WOOD OIL. J. Am. Chem. Soc. <u>56</u>, 899-901 (1934); C.A. <u>28</u>, 3052 (1934).

"The absorption characteristics of a- and β -eleostearic acids (I and II) are very similar, yet sufficiently different to enable them to be identified easily by this means. Although it is well recognized that light may cause profound changes in the acids, yet the light sources used in characterizing the acids had, under the conditions specified, no apparent action. A much stronger source, however, did cause very decided changes in the structure of I. I(15% soln. in 95% EtOH), irradiated for 2 hrs. under certain standard conditions, was converted into an acid that had the same absorption spectrum, in the region 2500 to 2850 A., as the acid obtained from the solid glyceride. It is possible to det. spectroscopically the percentage compn. of a mixt. of I and II." From C. A.

Eibner, A.

ISOMERISM IN FATTY OILS AND ITS TECHNICAL SIGNIFICANCE. Chem. Umschau Fette, Oele, Wachse u. Harze 29, 309-13, 317-21 (1922); C.A. 17, 1342-3 (1923).

"The possibility of isomers in mono-, di-, and simple and mixed triglycerides, and the minor isomerism due to the presence of an asymetric C atom are discussed and Hahn's formula for calcg. the possible no, of glyceride isomers is given. Sixteen isomers of oleic acid are possible, depending on the position of the double C-bond, none belonging to the drying acids. Fourteen isomers of linolic acid are possible; the 9, 10- to 12, 13-isomers form drying films of the poppy-oil type (ether-sol., melting on heating and easily cracking). Chinese wood oil contains eleostearic acid with 2 CH, groups between its 2 double bonds; it is this position that accounts for the extraordinary drying quality of wood oil. a-Eleostearic acid, m. 48°, is converted into the β acid, m. 72° by exposure to light in alc. soln. This phototropic property is unknown in other oils or acids. The clupanodonic acids are supposed to have only 1 CH2 group between their several double bonds, but this supposition needs verification. Acids of the castor-oil group contain the hydroxy group OH and their graphic formulas CH2(CH2)5 CH(OH)CH:CH(CH)8COOH (Krafft) or CH3(CH2)5CH(OH)CH2CH:CH(CH2)7COOH (Lewkowitsch) suggest the existence of the unsatd. acid CH3(CH2)5CH: CHCH:CH(CH2)7COOH, contg. two conjugated double bonds. No straightchain acid with less than 18 C atoms is a drying acid, excepting

isanic acid $(C_{1/4}H_{20}O_2)$ and the acids in chaulmoogra oil. The Bakelite procedure in making a film insol. and infusible appears analogous to the drying of linseed oil." From C. A.

Eibner, A., and Jung, V.

OXYNS. VII. THE DRYING OF FREE UNSATURATED ACIDS. Chem. Umschau Fette, Oele, Wachse u. Harze <u>38</u>, 267-73, 281-5 (1931)*; C. A. <u>26</u>, 858-9 (1932).

"a-Linoleic acid, m. 116-6.5°, dries slowly to a film with a max. wt. increase after 14 days, after 1 yr. it had not markedly yellowed nor re-softened, m. 170-180° with evolution of gas, turns dark red at 200°, becomes crystalline over CaCl2. a-Linolenic acid, m. 199.5-199.7°, becomes a dry film in 8-10 days, turns more yellow in winter than in summer, does not turn yellow in dry sir, browns at 100°, the film is tougher than that of linoleic acid, does not re-soften, in the quartz lamp light it turns to a dry film in 3 days, at 190-200° it turns red-brown. a-Eleostearic acid, m. 48-49°, forms a dry film in 6-8 days, turns less yellow than the linolenic acid film, but yellows strongly in the oven; the film loosens from glass in scales. Clupanodonic acid forms a dry film in 3 days, turns brown at room temp., does not re-soften, is easily removed from glass, becoming warm when the under side comes in contact with air, turns dark brown at 100° in 5 hrs.; toward H₂O it is the least stable of all films, turning milky, then swelling. Films with few double bonds dry slowly; those with many double bonds dry fast; the former, however, are more stable toward H₀O than the latter. Mulder has mentioned "white" oxynic acids, but has never obtained them; the above colorless films doubtless represent these "white" acids. When mixed with red lead or white lead to a paint the acids dry to a film in 1-4 days and when the films are exposed to H₀0 up to 4 days, they show an increasing susceptibility with increasing non-conjugated double bonds; hence clupanodonic acid (4 double bonds) is unfit as a paint material.

Oxynic acid film.	I no. (Hanus)	Acetyl. no. (Wolff)	%C	%H	%0	Mol. wt.
a-Linoleic acid	18.2-19.5	276.6-278	63.82	9.27	26.91	
a-Linolenic acid	20.6-21.2	278.5-287.9	60.55	8.4	31.05	826
a-Eleostearic acid	17.5-18.9	280.0-294.5	62.42	8.94	28.64	
Clupanodonic acid,					32.79	815.8
(ether-sol.)						
Clupanodonic acid,	7.76		62.87	7.7	29.43	1.086
(ether-insol.)				·		

The unsatd. acids dry to a film of oxynic acids which does not fully ripen, because of the absence of the glycerol radical, favoring thereby formation of hydroxy acids." From C. A. Eibner, A., and Rossmann, E.

CHINESE WOOD OIL. III. CONSTITUTION OF ELEOSTEARIC ACID. Chem. Umschau. Fette, Oele, Wachse u. Harze <u>35</u>, 197-9 (1928); Paint Varnish Production Mgr. 1929, 10-12 (Apr., 1929); G. A. <u>22</u>, 4839(1928).

"Eleostearic acid has 3 double bonds and when ozonized forms azelaic and valeric acids from the two end-members of its C chain from its central group glyoxal is formed. β -Eleostearic acid was ozonized in CHCl₃ soln. and the product decomposed by cold H₂O and addition of some SO₂. The presence of succinic acid could not be established. c-Eleostearic acid yielded as final ozonation products phenylnitrophenylosazone and glyoxal semicarbazone." From C. A.

Eigenberger, E.

ISOMERISM IN THE BETA-ELAEOSTEARIC ACID SERIES.

J. prakt. Chem. 136,75-116 (1933); Brit. Chem. Abstracts 1933, A, 375. "Hydrolysis of freshly-prepared β -elaeostearin (1) with EtOH-KOH containing a little water only) gives K β -elaeostearate (II); the acid obtained (in solution) under carefully defined conditions can be reconverted into (II), but the free acid, m.p. 71-71.5° isolated is a mixture. Crystallisation of (II) from 50% EtOH gives K Byelaeostearate (III) convertible into a Ag salt which with EtOH-KOH regenerates (III), which when crystallised from EtOH rearranges into (II); a K β₁-acid salt, C₁₈H₂₉O₂K, C₁₈H₃₀O₂, is described. Samples of (I) which have been allowed to autoxidise in the dark contain COMeo-sol. and -insol. material; hydrolysis of the insol. part with EtOH-KOH causes evolution of O_2 and gives K β_2 -elaeostearate (IV), also formed by autoxidation of (II) or (III); the β_2 -acid is produced when the above acid mixture is heated above the m.p. When the acid from (III) is heated at 250° in CO2, the resulting product sublimed, the sublimate extracted with light petroleum, and the extract evaporated in CO2, cryst. material is first obtained; the filtrate contains β_2 -elaeostearic acid, an oil (amorphous K salt, also formed when (III)² is heated to 210° vac.), which changes into the β_2 -acid on keeping. Numerous other interconversions are studied. A~corresponding series of Na salts is prepared. (IV) has the max. solubility and min. sp. conductivity in 94.6% (wt.) EtOH at 20° and 25° respectively; (II) has the max. conductivity and (III) has min. solubility." From Brit. Chem. Abstracts.

Farmer, E. H., and Paice, E. S.

UNSATURATED ACIDS OF NATURAL OILS. IV. THE HIGHLY UNSATURATED ACID OF TELFAIRIA OCCIDENTALES.

J. Chem. Soc. <u>1935</u>, 1630-2; C.A. <u>30</u>, 891 (1936).

"Freshly extd. oil from the kernels of <u>Telfairia occidentales</u> contains a-eleostearic acid m. 48°; after exposure to diffused light for some weeks very small yields of the β -isomer are isolated, the yield being greatly increased after exposure to ultraviolet radiation for some hrs. A sample of oil after standing 7 months gives 10% of the β -isomer. The solid material pptd. from the oil on standing is β -eleostearin." From C. A. Fritz, F.

CONSTITUTION OF ELEOSTEARIC ACID.

Farben-Ztg. 33, 1224-5 (1928); C.A. 22, 3629 (1928).

"A brief account of the work of various investigators on the constitution of eleostearic acid as revealed by its oxidation products. The validity of Böeseken and Ravenswaay's formula for the acid (C.A. 20, 44) is considered to be upheld." From C. A.

Greaves, J. H.

NEWER PRODUCTS AMONG THE DRYING OILS. Oil & Colour Trades J.109, 410, 412, 414 (1946); C.A. <u>40</u>, 3003 (1946).

"The only "new" oil arousing continued interest in recent years is is ano oil obtained from the fruit of <u>Ongokea klaineana</u>. Its drying properties are poor but it has 2 acetylenic linkages and a vinyl group, which affords great reactivity and which prevents the development of drying properties by heating the oil in bulk. Little known drying oils, botanically related to tung oil, such as <u>Garcia nutans</u>, have received some attention. Lesser consideration has been given to dehydrated castor, tung, and oiticica oils, tall oil, cashew nut-shell liquid and a few synthesized oils. The modification of linseed oil is discussed from the standpoint of: segregation, fatty acid modification and alc. modification. 27 references." From C. A.

Grun, Ad.

CHINESE WOOD OIL.

Z. angew. Chem. <u>39</u>, 381 (1926); C.A. <u>20</u>, 1912 (1926). "A criticism of the work of Nagel and Grüss (Z. angew. Chem. <u>39</u>, 10; cf. C.A. <u>20</u>, 1144)". From C.A.

Guedras, M.

RESEARCHES ON THE CHEMISTRY OF VARNISH.

Rev. gen. chim. 10, 93-100 (1907); C.A. 1, 1328 (1907). "This is a review of chemical investigations on linseed oil acids from Mulder, Hasura & Bauer, Coffignier, and others; of Cloez on the acids of tung oil, and of various writers on colophony and the metallic resinates. A few original experiments are described." From C.A.

Hilditch, T.P., and Pathak, S.P.

THE CATALYTIC HYDROGENATION OF METHYL ELEOSTEARATE, AND OF MIXTURES OF ELEOSTEARIC WITH OTHER POLYETHENOID LONG-CHAIN ESTERS.

Proc. Roy. Soc. (London) <u>A198</u>, 323-37 (1949); C.A. <u>44</u>, 2916 (1950). "The hydrogenation of the conjugated triene system present in Me eleostearate (9,11,13-octadecatrienoate) (I) has been compared with that of the pentadiene systems present in Me linolenate and Me linoleate. The course of the hydrogenation action in I has been followed spectrophotometrically. The primary action is the simultaneous addn. of 2 mols. of H to 1 mol. I and formation of very large proportions of ll-octadecenoic esters. Production of stearate does not occur to any marked extent until over 80% I has been

converted to the monoethenoid ester. The selectivity of the hydrogenation process has been studied in the cases of equimol. binary mixts. of I with, resp., Me cleate, lincleate, or linclenate. In a mixt. of I and oleate, hydrogenation of the latter does not set in until nearly all I has been converted to octadecenoate. With a mixt. of I and linoleate, the diene ester remains almost unattacked until 50% or more the I present has been converted into monoethenoid ester, after which it also commences to be transformed into monoethenoid esters. In a mixt. of I and linolenate, both esters undergo hydrogenation from the outset, but I disappears about twice as rapidly as the non-conjugated isomer. The activity to H of the double pentadiene system is comparable with that of the conjugated triene group in the I mol. The hydrogenation of Me linoleate in the presence of Raney Ni either at 110° or 170° is extremely selective, no Me stearate being produced until over 90% of the linoleate has been transformed into octadecenoates. The prepns. of the materials are described. The relative reactivities to H of eleostearate, linolenate, linoleate, and oleate are of the order 80:40:20:1. The pentadiene C system in linoleic ester and the doubled pentadiene arrangement in the linolenic series are relatively much more akin to the conjugated triene grouping than to an isolated ethylenic groups in their behavior with H in the presence of catalytic Ni. The studies have defined more clearly the course of hydrogenation of the eleostearic conjugated triene system, in which the primary phase consists almost wholly in the simultaneous addn. of 4 atoms of H to the eleostearate mol., with the production in 1 stage of a mono-ethenoid, or more probably a mixt. of isomeric monoethenoid, esters. Selectivity of hydrogenation is as well defined at the relatively low temp. of 110° as at higher temps., if the Ni catalyst is in a form which is suitably active at a low temp." From C. A.

Hu, Dju-Bin, and Wan, Sheng-Wu

KINETICS OF THE ICL ADDITION TO ALPHA-ELEOSTEARIC ACID.

J. Chinese Chem. Soc. 10, 83-9 (1943)*; C.A. 39, 454 (1945).

"The equil. const. K_B is celed. from concn. data and from the ratio $k_2:k_2$ ' giving values 20.2 and 20.8, resp. It is concluded that both the present value of K_2 and the theory of a reversible reaction (B) are well founded." From C. A.

Hulst, L.J.N. van der .

APPLICATION OF ABSORPTION SPECTRA IN FATTY OIL RESEARCH. II. Rec. trav. chim. <u>54</u>, 644-50 (1935); Brit. Chem. Abstracts <u>1935</u>, B, 912.

Absorption spectra " are applied to the quant. analysis of castor, sesame, and palm oils, also tung oil and its hydrogenation products. --The curve for tung oil hydrogenated under high pressure shows no max. at 230 mµ whence it is concluded that it contains no linoleic acid, eleostearic acid being transformed directly into oloic and stearic acids; at high temp./at 1 atm. linoleic acid is formed in quantity." From Brit. Chem. Abstracts. Ishio, M.

CONSTITUTION OF ELEOSTEARIC ACID.

J. Pharm. Soc. Japan <u>1926</u> (529), 21-5*; Chem. Zentr. <u>1926</u>, I, 3594. A review with experimental work on the oxidation of eleostearic acid and the examination of several of its derivatives.

Ishio, M.

CONSTITUTION OF ELEOSTEARIC ACID.

J. Pharm. Soc. Japan <u>1926</u> (529), 228-43*; C.A. <u>20</u>, 2819 (1926). "In order to settle whether or not eleostearic acid (I) contains $Me-(CH_2)_3CH=$ and = $CH(CH_2)_7CO_2H$, I. prepd. the dichloride (m. 88°), and decompd. it with O₃. a-Chlorocaproic acid (b₂104°), a-hydroxycaproic acid (m. 61°), a-chlorocaproic aldehyde (b₂₂ 60.5°), HCO_2H , CO_2 , and a mixt. of $HO_2CCHCl(CH_2)_7CO_2H$ and $OHCCHCl(CH_2)_7CO_2H$ are produced. This result shows conclusively that I has the 2 groups mentioned above. Next when dihydroeleostearic acid (II) was ozonized and decompd., caproic acid, HCO_2H , CO_2 , sebacic acid, and sebacic aldehyde were formed. This result must mean that II has $Me(CH_2)_4CH=$ and = $CH(CH_2)_8CO_2H$, or other groups which easily give

rise "to these groups." In order to det. this point and also harmoniously to interpret the result obtained from the O, decompn. of I, the nature of double bonds was analyzed. The detn? of mol. refractivity gives 98.62 for I, and 97.48 for II. The theoretical value for I should be 94.81 on the basis 3=, and 93.08 on basis of 2=, while that for II, should be 95.28 on the basis of 2=, and 93.54 on basis 1=; mol. exaltations are 3.81, 5.54 for I; and 2.20, 3.94 for II, and sp. exaltations 1.25, 1.81 for I, and 0.71 and 1.28 for Since the presence of multiple conjugated double bonds should II. show a sp. exaltation around 3.40, and simple conjugated double bonds 1.90, it is concluded that I has 2= of the conjugated type, and II has 1=. The I no. of I is 182.09, and that of II 90.32, which confirms the above conclusion. From these, I. proposes the constitution III for I and either IV or V for II. When II is incompletely oxidized by alk. KMnO, medium, 10,11,12,13-tetrahydroxy-stearic acid (m. 185°) is formed. ⁴If completely oxidized, caproic, oxalic and sebacic acids are formed, showing V to be the more likely structure for II.

Ivanoff, N.

NEOU OIL.

Bull. soc. chim. 11, 404-6 (1944); C.A. 40, 2323 (1946).

"The freshly pressed fixed oil (I) from <u>Parinarium macrophyllum</u> (Neou oil) gave the following consts.: n^O 1.4901; d²⁰ 0.910 changing after 2-3 months' standing to 0.932), Hanus I no. 140-4, Wijs I no. 130-40, thiocyanogen no. 78-9, diene no. 25.5, sapon. no. 184, Hehner no. 94, unsaponifiable substances about 1%. Acetylation and hexabromide tests proved neg. After sapong. I and extg. the free acids with petr. ether contg. a trace of I, β -<u>eleostearic</u> acid (II) m. 71.5° was obtained (further identified by the NH, salt, m. 108-10° (decompn.) and the K salt from which II was readily regenerated). For identification and comparative purposes, II was also isolated by Rossman's method (C. A. 27, 702) from China wood oil, but in this latter case the a-isomer (III) of II, m. 47°, could be isolated prior to its isomerization into II, whereas III could never be actually identified among the acids from I. This inability to isolate III (which was reported as a sapon. product of I by Brown and Farmer, (C.A. 29, 6085) is discussed briefly. Besides 28.2% II, the fat acids obtained on sapong. I included 20.1% oleic, 34.3% linoleic, and 11.4% satd. acids. These data agree closely with those reported by Steger and van Loon (C.A. 28, 2929) who were uncertain about the identity of II." From C. A.

Kametaka, T.

COMPOSITION OF SO-CALLED ELAEOMARGARIC ACID.

J. Chem. Soc. <u>83</u>, 1042-1045 (1903); J. Soc. Chem. Ind. <u>22</u>, 1138 (1903).

"The solid fatty acid of the oil of Elaeococca vernicia, or Japanese wood oil, was prepared by saponification with alcoholic potash, followed by treatment with hydrochloric acid. After recrystallisation from alcohol, the acid was obtained in the form of white, lustrous laminae, melting at 43°-44°C. The bromineaddition and exidation products of the acid were prepared by Hazura's methods (Monatsh. für Chem., 1887, 8, 148; and this Journal, 1888, 506). The bromine-addition product had the composition C18H32O2Br4; it melted at 114°C., and appeared to be identical with the product obtained from linolic acid. Two oxidation products were obtained: (1) an acid, C18H32(OH)402, melting at 1710-172°C., and agreeing with sativic acid; and (2) an acid, C18H24(OH)202, melting at 126°C., and consisting, probably, of impure dihydroxystearic acid. The author concludes that the solid acid, which Cloëz (Comptes rend., 1875, 81, 469; 1876, 82, 501, 83, 943) named elaeomargaric acid, and for which Maquenne (Comptes rend., 1902, 135, 696) recently proposed the name *c*-elaeostearic acid, has the composition C18H32O2, and is a sterecisomeride of linolic acid. (See elso this Journel, 1896, 661; 1897, 195, 684; 1898, 305, 674, 772; 1899, 283; and 1900, 156)." From J. Sc. Chem. Ind.

Kametaka, T.

CONSTITUTION OF ELAEOMARGARIC ACID.

J. Coll. Sci. Imp. Univ. Tokyo 25, (Art.3), 1-8 (1909).

"The acid was treated with $KMnO_{4}$, KOH or PhNH₂ and the reactions were examined but no definite conclusion was reached. The acid was also treated with conc. H_2SO_4 ." From C. A.

Kappelmeier, C.P.A.

OITICICA FAT AND ITS FUNDAMENTAL DIFFERENCE FROM CHINA WOOD OIL. Fettchem. Umschau 42, 145-52 (1935); Verfkronick 8, 279-83 (1935); C.A. 30, 887 (1936).

"Various samples of oiticica fat (I), obtained either direct from Brazil or extd. from freshly ground nut kernels preferably with ether or benzene or, less suitably, with petr. ether, had the following consts .: acid no. 2-8, sapon. no. 187-193, I no. (Wijsafter reacting 2 hrs.) 140-150. Ac no. 30-40, hexabromide test neg., gelatination temp. 260-70°, d²⁰ 0.9670-80, n²⁰ 1.5140-80, n_f - n_c (dispersion) 0.0170-0.0185. (Since I ordinarily has a buttery consistency, the last 3 consts. were detd. on melted, super-cooled samples -- a procedure which is not recommended.) Removing the break from I by rapidly heating to 200° and then centrifuging failed to prevent I from reassuming its buttery consistency at room temp., although this can be prevented by converting I into stand oil by heating to 225-50°. β -Couepic acid (II) was prepd. by first adding a small amt. of I to a benzene soln. of the free fatty acids of I and then exposing to direct sunlight. The fine leaflets of II, which sepd. out, m. 101-2° after recrystn. from acetone and vacuum drying. The ketone group in HI, which was revealed by the formation of a semicarbazone, m. 134-7, seems to have a disturbing effect on acidimetric titrations and also on I no. detns. Whatever the cause, the apparent I no. of II (Kaufmann method) increased from 194 to 332 and a small amt. of free acid appeared on increasing the time of halogenation from 2 to 190 hrs. Hydrogenation studies offer more promise in this field than halogenation expts. K-B-couepate is a stable, cryst. salt, whose ready crystn. from alc. sapon. mixts. aids greatly in detecting II. Ammonium- β -coupate m. 127° and gives no color with FeCl₂ soln. Catalytic hydrogenation converted II into hexahydrocouepic acid (III) which yielded a semicarbazone m. 135.5°. Me- β -couepate (IV) m. 41°, and behaved like II when halogenated. A comparison of the consts. of IV and of freshly prepd. samples of the Me esters of α - and β -eleostepric acid confirmed the non-identity of IV with either of the latter. Nevertheless I may contain varying amts. of eleostearic acids (cf. van Loon and Steger, C.A. 25, 4848). A mixed m.p. indicated that IV is identical with the hexahydrolicanic acid of Brown and Farmer (C.A. 29, 5294). K. criticizes Rossmann's theory (C.A. 26, 2416) that only 2 geometrically isomeric eleostearic acids can exist." From C. A.

Kass, J.P., Nichols, J., and Burr, G.O.

CERTAIN DERIVATIVES OF THE OCTADECENOIC ACIDS. I. THE P-PHENYLPHENACYL ESTERS. II. THE S-BENZYLTHIURONIUM SALTS. J. Am. Chem. Soc. 64, 1061-2 (1942); C.A. <u>36</u>, 4095 (1942).

"This study was an attempt to find methods for characterizing unsatd. fatty acids. <u>p-Phenylphenacyl esters</u> were prepd. by the method of Drake and Bronitsky (C.A. 24, 5030); a slightly acid (HCl) soln. of the fatty acid and a slight excess of p-PhC₆H₂COCH₂Br in EtOH were boiled in a N atm. for 1 hr. and the product crystd. 3-7 times from Me₂Co; oleic (I), m. 61-2°, I no. 52.5 (calcd. 53.3); elaidic (II), m. 72-3°, I no. 52.8 (53.3); <u>linoleic</u> (III), m. 37-7.5°, 46.5-7°, I no. 99.6 (107); <u>linolelaidic</u> (IV), m. 73-5°, I no. 83.2 (107); <u>linolenic</u> (V), m. 37.5-8, 38-9°, I no. 140.4 (161.2); β-<u>eleostearic</u> (VI), m. 89-90°; 9,10,12,13-<u>tetrabromostearic</u> (VII), m. 107-8°; the derivs. of III and V appear to be liquid crystals, melting to an opaque liquid at the lower temp. and clearing suddenly at the higher temp. Although all had good m. ps., only the esters of I and II were found to have the calcd. I nos. among the unsatd.

derivs. The S-benzylthiuronium salts were prepd. by the method of Donleavy (G.A. 30, 5912): I, m. 134-4.5°, I no. 59.7 (56.1); II, m. 125-5.5°, I no. 66.6 (56.1); III, m. 123.5-5°, I no. 108.2 (113.7); IV m. 122-3°, I no. 100 (113.7); V, m. 122-4°, I no. 160.2 (171.4); VI, m. 115-30°; VII, m. 129-30°. These salts were not suitable for identification purposes because of impurity, instability, similarity of m.p. and dependence of the m.p. on rate of heating. The appearance of these derivs. varied from cryst. to noncryst. with the diminishing m.p. of the parent acid. An improved procedure, avoiding the formation of mercaptans, is given for the recovery of the acids from these salts." From C. A.

THE

Kaufman, H. P., and Wolff, W. THE USE OF MOLECULAR DISTILLATION IN THE FIELD OF FATS. I. DISTILLATION OF FAT ACIDS AND THE REFINING OF FAT. Fette u. Seifen 47, 252-61 (1940); C.A. 35, 4981-2 (1941). In a molecular still at 10-3-10-4 mm. Hg. B-eleostearic acid distilled without decomposition.

Kodicek, E., and Worden, A.N. EFFECT OF UNSATURATED FAT-ACIDS ON THE ACID PRODUCTION OF LACTOBACILLUS HELVETICUS.

Nature 157, 587 (1946); C.A. 40, 4766-7 (1946).

"a-Eleostearic acid in concns. of 16/y per 10 ml. medium depressed the acid production of L. helveticus considerably for 48 hrs., whereas the <u>trans</u>-isomer, β -eleostearic acid, was without inhibitory activity. When lactobacilli were grown aerobically in presence of oleic acid and elaidic acid, resp., the oleic acid inhibited growth and acid production completely for the 1st 24 hours. Elaidic acid did not show any inhibiting effect." From C. A.

Kurata, M., and Miyoshi, S.

THE DIENE COMPOUNDS. III. THE ADDITION PRODUCT OF BETA-ELEOSTEARIC ACID AND ACROLEIN.

J. Chem. Soc. Japan <u>63</u>, 1158-9 (1942)*; C.A. <u>41</u>, 3755 (1947).

"The addn. of B-eleostearic acid and acrolein has been studied. β-Eleostearic acid (60 g.) and 14.4 g. acrolein heated in a sealed tube at 130-140° 2 hrs. give a brown viscous product, yielding on fractional distn. 9 g., b7 247-52°, n_D^{25} , 1.4900, d_1^{15} 0.9844, iodine value 155.2, neutralization value 168.1. This compd. is found to have the structure (OHC) HC.CH2.-CBu:CH.CH:CH.CHCH(CH2)7CO2H." From C. A.

Loon, J. van.

THE APPARENT IODINE NUMBER OF ELEOSTEARIC ACID. Chem. Umschau Fette, Oele, Nachseu. Harze 37, 269-71 (1930); C. A. 24, 6045 (1930).

"As with Chinese wood oil (C.A. 24, 4413) L. finds that the β eleostearic acid itself has an I no. which varies with the duration of exposure to I and with the excess of I used. The I absorption curve also shows a decided break at 180 I no., indicating a tetraiodide which upon long-continued I action becomes finally

a hexaiodide. The a-eleostearic acid adds the halogen more rapidly than the β acid; apparently another unknown acid is present which is highly unsatd. Using L's method of examn., W. C. Smit finds that the conjugated 9,11-linoleic acid which comes close to the eleostearic acid in the position of the double bond shows an I curve parallel to that of eleostearic acid." From C. A.

McKinney, R.S., and Jamieson, G.S.

JAPANESE TUNG OIL.

Oil & Soap 14, 2-3 (1937); Brit Chem. Abstracts 1937, B, 940.
"The kernels formed 63.9% of the seeds of <u>Aleurites cordata</u> and contained '67.5% of oil. The expressed oil, which did not gel in the Browne heat test, but solidified on treatment with SbCl₃ in CHCl₃, had d²₂ 0.9313, n²⁵ 1.5059, acid val. 0.6, sap. val. 190-2, J val. (Rosenmund-Kuhnhenn, 1/2 hr.) 145.2, SCN val. 80.9, saponiable matter (I val. 105.5) 0.57%. The oil contains about 70.5% of elaeostearic acids, 18.5% of oleic acid, and 6.2% of saturated acids (Bertram). No evidence of linoleic or linolenic acid could be found. Allowing 1/2 hr. for reaction, the Rosenmund-Kuhnhenn method gives I vals. for the oil or for pure β-elaeostearic acid (I) (viz., 182.4 = 2 double linkings) which are independent of the amount of oil used for the test. The SCN val., 91.2, of pure (I) corresponds with one double linking." From Brit. Chem. Abstracts.

Majima, R. (also given as Majenia, R.)

CONSTITUTION OF ELEOSTEARIC ACID.

Ber. 42, 674-680 (1909); J. Soc. Chem. Ind. 28, 316 (1909); C.A. 3, 1159 (1909).

"Kametaka (this J., 1138, 1903) obtained the same tetrabromide and tetrahydroxy acid (sativic acid) from elaeostearic acid as from linolic acid, and therefore concluded that the two acids were isomeric. To obtain further information of the constitution of elaeostearic acid, the author has used ozone as an oxidising agent in a similar manner to that employed by Harries and Turk (this J., 1158, 1906) with oleic acid. He has found that elaeostearic acid absorbs 2 mols. of ozone, which supports the view that it contains 2 double linkages. The di-ozonide was an amorphous yellowish, semi-solid substance with the composition C18H3208. When boiled with water it was readily decomposed, the products of decomposition including n-valeric aldehyde, n-valeric acid, the semi-aldehyde of azelaic acid, and azelaic acid. A substance that appeared to be succinic di-aldehyde was isolated, but neither succinic acid nor its semi-aldehyde could be identified, and if present could only have been there in small quantity. The nature of the decomposition products supports Maquenne's view that elaeostearic acid contains double linkages between the fifth and sixth and the ninth and tenth carbon atoms as represented in the formula -- CH2. (CH2)2. CH: CH. (CH2)2. CH:CH. (CH2)7.CO2H. The elaeostearic acid prepared from tung oil by Kametaka's method distilled almost unchanged in a current of carbon dioxide at about 235 degrees C. under a pressure of 12 mm, leaving in the flask an amorphous (probably polymerised) residue amounting to about 1/7 to 1/5 of the original substance." From J. Soc. Chem. Ind.

Majima, R. (also given as Majenia, R.).

CHIEF CONSTITUENT OF JAPAN LAC. III. URUSHIOL. CATALYTIC REDUCTION OF JAPAN LAC.

Ber. 45, 2727-30 (1912); J. Soc. Chem. Ind. 31, 998 (1912).

"Catalytic reduction of urushiol from Japan lac (this J., 1245, 1907; 532, 1212, 1909), by the method of Willstätter (this J., 642, 829, 1908) with hydrogen and platinum black, yielded crystals of hydro-urushiol, $C_{20}H_{34}O_2$, which melted at 58° to 59°C. after recrystallisation from hot xylene.---Elseostearic acid:-- Catalytic reduction of elaeostearic acid from tung oil gave an almost quantitative yield of stearic acid, thus proving the normal linkage of the carbon atoms in the original acid (see this J., 316, 1909)." From J. Soc. Chem. Ind.

Manecke, W., and Volbert, F.

SPECTROSCOPIC DETERMINATION OF THE CONSTITUTION OF THE FATTY ACIDS OF TUNG OIL.

Farben-Ztg. 32, 2829-31, 2887-9 (1927); C.A. 22, 2478 (1928).

"M. and F. give a review of the various methods of detg. the constitution of the eleostearic acid in tung oil. They det. the spectroscopic absorption of this acid with the method of V. Henri and find an absorption figure which is higher than that of linoleic acid. Considering the fact that an increase in the absorption goes parallel with an increase in double bonds, they conclude that the eleostearic acid contains more than 2 double bonds." From C. A.

Maquenne, L.

THE COMPOSITION AND THE CONSTITUTION OF ELEOSTEARIC ACID. Bull. soc. chim. 33, 1654-5 (1923)*; C.A. 18, 660 (1924).

"In connection with the formula proposed by Vercruysse (cf. C.A. 17, 2265) for eleomargaric acid, confusing it with eleostearic acid (cf. Kametaka, J. Chem. Soc. 83, 1042 (1903); M. calls attention to his earlier work (Compt. rend. 135, 696 (1902), proving that the formula of eleostearic acid is $C_{18}H_{30}O_2$." From C. A.

Miller, A.B., and Claxton, E.

ATMOSPHERIC OXIDATION OF METHYL AND GLYCOL ESTERS OF BETA-ELEOSTEARIC ACLD.

Ind. Eng. Chem. 20, 43-8 (1928); C.A. 22, 943 (1928).

"Studies which have been made of the phys. and chem. changes which take place upon oxidation of β -eleostearic acid (I) and its Me, glycol, and glycerol esters, indicate the formation of polymers contg. considerable added 0 and condensed split acid. An important function of the valency of the alc. is the stability it imparts to the ester, thus detg. the tendency to split off I, which through condensation and aggregation of its long C chains actively influences gel formation." From C.A.

Miller, A.B., and Rohrbach, K.L.

ATMCSPHERIC OXIDATION OF ESTERS OF BETA-ELEOSTEARIC ACID WITH MONOHYDRIC ALCOHOLS.

Ind. Eng. Chem. <u>21</u>, 338-42 (1929); C.A. <u>23</u>, 2151 (1929). "The following esters of β-eleostearic acid were prepd. by esterification of β-eleostearic acid (I), m. 45° (prepd. from American tung oil), and the corresponding alc, with dry HCl as condensing agent: Me; Pr, light yellow oil n_D^{25} 1.4962; iso-Pr, dark oil, n_D^{25} 1.4940; Bu, dark oil, n_D^{25} 1.4947; benzyl, dark oil, n_D^{25} 1.5312. These esters oxidize rapidly (cf. C.A. 22, 943) and completely similarly to the esters of polyhydric alcs. but without drying; splitting forms simpler acids having a tendency to add to the ester mol; hydrolysis with the formation of I occurs to a limited extent. Associates of several mols. of oxidized ester are usually dissolved in a dispersion of simple oxidized mols.; the acid set free from exidized esters are mostly di- and polybasic. There is little neutral and no acid hydrolysis and since these esters form abundant strong acids on oxidation, hydrolysis is inhibited in an acid medium. The consts. of the end products vary with the no. of C atoms in the straight-chain alc. esters and are regularly higher or lower in the case of isopropyl and benzyl ester; this is attributed to the relative tendency of the esters to hydrolyze on oxidation, producing I. The Me ester oxidized in the presence of I gels, the acid forming an addn. product with the ester (stearic acid does not combine under these conditions). These results confirm the hypothesis that an important function of the alc. group in the esters of I is the stability imparted to the ester, thus detg. the tendency to split off I, which, because of addn. and aggregation of the long C chains, actively influences gel formation." From C. A.

Miyoshi, S., and Ibuki, E.

THE DIEME COMPOUNDS. II. THE AUTOXIDATION OF UNSATURATED FAT ACIDS.

J. Chem. Soc. Japan <u>63</u>, 1151-7 (1942)*; C.A. <u>41</u>, 3755 (1947).

"The autoxidation of oleic acid and elaidic acids and their Me esters, of a-and β -eleosteeric acids, and of soybean oil has been studied. The order of the velocity of autoxidation is found to be oleic acid > elaidic acid > Me oleate > Me elaidate. The amt. of 0 absorbed by a-eleosteeric acid (cis form) is 281 times that absorbed by oleic acid. The change in the amt. of 0 absorbed by soybean oil with the solvent used for extn. is found to be total alc. ext. > solid part of alc. ext. > benzene ext. > ether ext. > liquid part of alc. extract." From C.A.

Morrell, R. S.

THE TRANSFORMATION OF METHYL ALPHA-ELEOSTEARATE INTO METHYL BETA-ELEOSTEARATE.

J. Soc. Chem. Ind. 37, 181-2T(1918); C.A. 13, 130 (1919).

"Chinese wood oil, d. 0.944, n_D 1.5171 (12.5°), was thickened at 240° for 20 min., cooled rapidly, and treated with acetone. The thickened oil had d. 0.9638 (15°) and a mol. wt. cf 1431 (in C₆H₆). Both the sol. (polymerized) part "A" and the insol. part "B" were transformed into Me esters by NaOMe (Bull's method). The Me ester from "A" had d₁ 0.9159, n¹⁰ 1.4958, mol. wt. (in C₆H₆) 300; I value 151.8 (1.5 hrs.), 178 (6 days). The Me ester from "B" had d₁₂ 0.936; n¹² = 1.49850; I value 138 (1.5 hrs.) 168 (6 days); mol. wt. $(C_{0}H_{6})$ 393. The Me esters were fractionated under 10 mm. The Me ester from "A", redistd. between 209° and 224° and sapon. in the cold, gave an acid, m. 66-9°, which on thrice recrystg. from 60% alc. gave β -eleostearic acid, $C_{18}H_{32}O_2$, m. 71-2°, I value 172. The Me ester from "B" treated the same way gave an acid of practically the same properties. Examn, of the Ce salt from the undistd. Me ester obtained from "A" showed that a-acid was present almost entirely and no β -acid. The conclusion is drawn that stereoisomeric change has occurred during distn. of the ester although NaOMe or polymerization may be factors in the transformation of Me a-eleostearate into the β -ester." From C. A.

Morrell, R. S.

THE TRANSFORMATION OF METHYL ALPHA-ELEOSTEARATE INTO METHYL BETA-ELEOSTEARATE.

J. Soc. Chem. Ind. 41, 328T (1922); C.A. <u>17</u>, 267 (1923). "Bauer and Herberts (C. A. <u>16</u>, 3550) failed to acknowledge M's earlier work (C.A. <u>13</u>, 130) on this transformation." From C. A.

Morrell, R. S.

CHEMISTRY OF DRYING-OIL FILMS.

Chemistry & Industry <u>56</u>, 795-8 (1937); C.A. <u>31</u>, 8224, (1937). "Exama. of cryst, β-eleostearin obtained from tung oil by irradiation has advanced the study of the polymerization of "oxyns" from drying oils. Upon oxidation of this substance, there are marked differences in the activity and character of the peroxide according to the position of the parent double linking, the remote linking having basic and the near linking having acidic properties. Nonpolar solvents, as CCL and benzene, require an induction period, while in glacial acetic acid soln. the oxyn polymerization is more rapid. M. favors the opinion that in benzene soln. mol. aggregates are formed by assocn., while in acetic acid soln. a peroxide of dimeride character is formed." From C. A.

Morrell, R. S., and Davis, W. R.

RECENT INVESTIGATIONS INTO THE DRYING OF OILS AND RELATED UNSATURATED COMPOUNDS.

Trans. Faraday Soc. 32, 209-19(1936); C.A. 30, 2777-8 (1936).

"Examn. of the at. models of the 8 possible cis-trans isomers of eleostearic acid and a study of their reaction with maleic anhydride gives the a-acid the arrangement T-C-C and the β -acid the arrangement C-C-T, where C is cis and T is trans. The effects of polar and nonpolar solvents and of oxidation catalysts on the mol. aggregation of the oxidation products of maleic anhydride compds. of the 2 acids were noted. Peroxides were produced at the remote double bonds only with the β -acid. Tautomeric keto-hydroxy compds. were formed with the a-acid, and the ring double bonds were not attacked but were oxidized to the keto-hydroxy form. Assocn. of the peroxide takes place, but not in the a-compds. or in the ring double bonds of the β -varieties. Peroxides in nonpolar solvents formed mol. aggregates, owing to the potential of the remote double bonds together with the addn. of the strongly polar peroxide group. In the polar solvents, β -compds. show assocn, due to the combination of primary valences from the peroxide group, as indicated by the increased viscosity of the soln. corresponding to a fall in peroxide value, probably due to gradual decompon. of peroxide aggregates to chain-like polymers of oxides. This accounts for changes occurring in the aging of drying oils, and the disappearance of bloom, which is ascribed to free peroxide groups. The properties of β -eleostearin maleic anhydride are so similar to those of oil varnishes, especially tung oil, that they can probably be used to study varnishes. The rate of oxidation and the character of the product are closely connected with the structure of the oil and especially with the positions of the double bonds in its con-

Morrell, R. S., and Marks, S.

THE POLYMERIZATION OF DRYING OILS.

stituent glycerides." From C. A.

J. Oil & Colour Chemists' Assoc. 13, 84-90 (1930); C.A. 24, 2901 (1930).

"When detd. in associating liquids such as C₆H₆, the mol. wt. of drying oils is greater than when detd. in dispersing liquids such as CCl₄. Iodine values also depend upon the dispersing properties of the solvent in which they are detd. The authors favor an assocd. structure for heat-bodied oils and a macro-mol. structure for oxidized oils." From C. A.

When β -eleostearic acid is oxidized and the ether-insoluble gel, which is thereby produced, is methylated, two methyl esters are obtained; one is insoluble in petroleum ether (MEA) and the other soluble (MEC). The proportions of these two esters depend on the degree of methylation. The molecular weights of MEA in acetic acid were 444-661 while in benzene they were 1280-2114 indicating association. MEC showed less change being 367-387 in acetic acid and 353-444 in benzene. MEA gave a high iodine value, possibly because of a rearrangement from -CH-CH- to -C=C-.

1

0 0

9

OH OH

Morrell, R. S., and Samuels, H.

DOUBLY CONJUCATED SYSTEM IN ALPHA- AND BETA-ELEOSTEARIC ACIDS. J. Chem. Soc. <u>1932</u>, 2251-4; C.A. <u>26</u>, 5545 (1932).

"β-Eleostearic acid and maleic anhydride (I) give an addn. compd., $C_{22}H_{32}O_5$, m 77°; oxidation with KMnO, in Me₂CO gives valeric acid and a brown tar; further oxidation of ² the latter gives some azelaic acid (II). The α-acid and I give an addn. compd., m. 62.5°; oxidation gives 36% of II and a tar, which on further oxidation gives a mixt. of II and $C_5H_{10}O_2$. The formation of these products of oxidation of the tars can be explained by the complete disruption of the non-sym. 6-ring acids. There was no reaction between I and coumarin, vinyl acetate, anthraquinone, acrylic acid and citraconic anhydride; $O:C_6H_4:O$ shows a violent reaction, giving a black sirup, probably an 'oxidation product of the conjugated substance. I and Me β-eleostearate give an addn. Nagel, W., and Gruss, J.

CHINESE WOOD OIL.

Wiss. Veröffentl. Siemens-Konzern 4, 284-320(1925); Brit.Chem.Abstracts 1926, A, 498.

"The following derivatives of α -elaeostearic acid are described: potassium, sodium and copper salts; methyl ester, b.p. 214°/12 mm. (with conversion into the β -isomeride, η°_{25} 0.109 (as compared with 2.019 for the tung oil,) obtained by the action of diazomethane on the acid or of methyl-alcohol potassium hydroxide on the original tung oil; ethyl and isoamyl esters prepared in a similar manner, b.p. 229-232°/17.5 mm. and 260-280°/40-70 mm. (decomp.)respectively; glycol ester (β -hydroxyethyl ester) decomposed on distillation, obtained by heating the acid with ethylene glycol at 180-200°. The following derivatives of β -elaeostearic acid are described: amide m.p. 111-112°, hydrazide, m.p. 128-129°, obtained from the methyl ester; ethyl ester, b.p. 225-240/15 mm." From Brit. Chem. Abstracts

Noller, C.R., Carson, J.F., Martin, H., and Hawkins, K.S. RELATIVE RATES OF OZONATION OF UNSATURATED COMPOUNDS.

Am diam day 50 21 6 (1026), (1 A 20 1020 (102)

J. Am. Chem. Soc. <u>58</u>, 24-6 (1936); C.A. <u>30</u>, 1739 (1936).

"Curves are given showing the relative rates of ozonation of a no. of unsatd. compds. Whereas a double bond, unaffected by the presence of other groups, adds O2 extremely rapidly, the rate is markedly decreased when the double bond is conjugated with CO groups; 3 or more Ph groups or 2 Cl atoms attached to the doubly bound C atoms also decrease the rate of addn. Where 2 or 3 double bonds are conjugated with each other, 1 bond adds 0, rapidly while the others add only slowly. In the case of cis-trans-isomers, where the rate of addn. is decreased by other groups, the trans- is found to add more rapidly than the cis-form. The procedure should prove valuable in the investigation of unsatd. compds. of unknown structure. Compds. studied include oleic acid, Me oleate, elaidic acid, 1-phenyl-1cyclohexene, (ClCH:), (Ph₂C:), Ph₂C:CHPh, stilbene, vinylacetic acid, crotonic acid, cinnamic acid, crotonicaldehyde, itaconic acid, diphenylbutadiene, eleostearic acid, sorbic acid, citraconic acid, Me maleate, maleic acid, mesaconic acid, and Me fumarate." From C.A.

Overholt, J.L., and Elm, A.C.

FORMATION AND DETERIORATION OF PAINT FILMS. CHANGES IN FILMS OF METHYL ESTERS OF SEVERAL UNSATURATED FAT ACIDS UNDER EXPOSURE OF ULTRAVIOLET LIGHT.

Ind. Eng. Chem. 32, 378-83 (1940); C.A. 34, 2617 (1940).

"Films of the Me esters of oleic, linoleic, linolenic and eleosteeric acids were exposed to ultraviolet light in a const.-temp. room at 65% relative humidity and 25°. At intervals samples of the exposed esters were analyzed for change in wt., degree and type of unsatr., degree and type of oxidation, ultimate analysis, mol. wt., viscosity, d. and n. Changes in the above properties during the 1st 1000 hrs. are shown by a series of graphs. The esters gain wt. during the 1st stages of exposure proportional to their unsatr. and later lose wt. owing to decompn. The I addn. values give indications of a 3-stage drying process: an induction stage, a stage of rapid decrease in unsath. which corresponds to the max. in peroxide content and a less definite stage with uncertain results. The highest peroxide concerned present at any time even in Me linoleate is equiv. to only a fraction, of one double linkage. OH reaches its max. after the peroxides have started to decompose. Mol. wts. measured in C_{6H_6} and tert-BuOH show that the eleostearate passes through a max. shortly 'before its max. peroxide concerned is observed. There is little change in mol. wts. of the others although viscosity increases to 100 times the original value." From C. A.

Overholt, J.L., and Elm, A.C.

FORMATION AND DETERIORATION OF PAINT FILMS. CHANGES IN FILMS OF GLYCOL ESTERS OF SEVERAL UNSATURATED FAT ACIDS UNDER EXPOSURE TO ULTRAVIOLET LIGHT.

Ind. Eng. Chem. <u>32</u>, 1348-51 (1940); C. A. <u>34</u>, 8300 (1940).

"Changes taking place in the films of glycol oleate, linoleate, linolenate and eleostearate, when subjected to ultraviolet light, are evaluated by the methods previously described for the Me esters (C. A. <u>34</u>, 2617). The oxidation of the glycol esters follows similar lines to the oxidation of the Me esters. Glycol eleostearate is pasty at room temperature and does not give clear films. The linoleate sets to a tack-free infusible film in about 10 hrs., which resembles a typical drying-oil film. The eleostearate changes, first, in 3-6 hrs. to a wrinkled mass similar to a badly frosted tung-oil film and then after 200 hrs. to a sticky, highly viscous material. The most striking difference between the glycol esters and the Me esters was shown in the rate of viscosity increase during exposure. The glycol ester curves are smoother; the sudden upturn indicating that gelation or solidification occurs earlier." From C. A.

Planck, R. W., Pack, F.C., and Heinzelman, D.C.

STABILITY OF ELEOSTEARIC ACID DURING STORAGE.

Proc. Am. Tung Oil Assoc. 1950, 37-46.

"Samples of freshly-prepared a- and B-eleostearic acids have been stored under varying conditions of temperature, light, air and solvents. and the amounts of unchanged eleostearic acid determined by spectrophotometric examination. Exposure of the dry crystalline acids to the air at temperatures from 4° to 35°C. resulted in their conversion into viscous liquid products only partially soluble in cyclohexane. Storage at 4°C. improved the stability of the a-eleostearic acid exposed to air. The β -isomer was quite stable under these conditions. No measurable changes occurred in the a-acid when stored at -40°C. in the presence of air. The influence of light on either acid is relatively slight. Samples stored in evacuated apoules in the presence or absence of light at temperatures from -40° to 35°C. were quite stable. β -eleosteatic acid, made into pastes with ethanol and stored in completely filled containers, generally was stable both in the presence and absence of light at temperatures from 4° to 35°C. Ethanol solutions of α -eleostearic acid refluxed for one hour and β -eleostearic acid refluxed for 23 hours showed no change in composition." Summary by the authors.

Rinkes, I. J.

ADDUCT OF BETA-ELAEOSTEARIC ACID AND MALEIC ANHYDRIDE.

Rec. trav. chim., <u>62</u>, 557-560 (1943) (in German); Brit. Chem. Abstracts <u>1945</u>, A, II, 182.

"The structure CH•CH [CH2]7•CO2H)•CH•CO 0, assigned to the adduct CH•CH(CH:CHBu^a) - CH•CO

(I) from elaeostearic acid (II) and (:CH•CO)₂O (III) by Morrell et al. (A., 1018, 1932,) is confirmed. (I) and (II) at 80-105° give (III), which passes when heated with dry Ba(OH)₂ and Zn dust at 360-400°/10-15 mm. into p-hexylheptylbenzene (IV), b.p. 185-187°/10 mm., m.p. - 40°, oxidized by KMnO₂ or, better, by CrO₃ in AcOH to $p-C_{6H_2}(CO_{2H_2})$, identified as the Me₂ ester. n-C₇H₂·OH is transformed by ZnCl₂-NH₂Ph at 270° into p-n-heptylaniline, b.p. 159-160°/10 mm., m.p. 4°, converted in the usual monner into p-iodo-n-heptylbenzene, b.p. 165°/10 mm. This with n-C₆H₂I and powdered Na under light petroleum gives (IV), m.p. - 32°." Brit. Chem. Abstrects.

Rossman, E.

ELEOSTEARIC ACIDS. I. ISOMERISM OF THE ELEOSTEARIC ACIDS. Chem. Umschau Fette Oelc, Wachse u. Harze <u>39</u>, 220-4 (1932); C.A. <u>27</u>, 702 (1933).

"cis-trans-Formation: The cis-form of a-eleostearic acid of wood oil with its 3 double bonds, is easily transformed into the β - or trans-form by light, high temp., I or S, more slowly by mineral acids. at 220° or below no isomerism occurs, but above 255° it takes place almost instantaneously. When distg. a-esters in high vacuum, polymerization results below 230° and isomerization above 230°. trans-cis-Formation: All attempts to change the β -form back into its α -form by heat, distn., etc. have failed; only the β -form plus liquid by-products resulted. A tabulation of properties of the various eleostearic acids is given. The β -acid crystallizes easily, the a-acid tends to remain liquid, probably because the former has a 1-dimensional plane formation while the latter is a 2-dimensional space mol., so that wood oil may be considered a liquid stable, undercooked triglyceride, a liquid resin type; this would explain its high viscosity at room temp. Attempts to synthesize the a-triglyceride have always yielded the g-glyceride plus polymerized products. Couppinic acid is probably not an isoeleostearic acid. Directions are given for the prepn. of eleostearic acids and their esters." From C. A.

Rouzier

ELEOSTEARIC ACID.

Diplôme d'Etudes Superieures, Marseille, 1936*.

Schapringer, S. von

ON THE CONSTITUTION OF WOOD OIL ACID AND THE POLYMERIZATION OF WOOD OIL. Thesis, Technical High School, Karlsruhe, 1911.

Research was carried out on an oil from the seeds of <u>Aleurites</u> <u>cordata</u> with the following constants: d, 0.94417; sap. value, 194.8; I no. 159.21; n_D, 1.5923. Oxidation of wood oil acids (elaeomargaric)

with KMnO, gave sativic acid, a little azelaic acid and some dihydroxystearic acid (probably from oleic acid), thus confirming Kametaka's view that elaemargaric belongs in the linolic acid series. Oxidation with O2 gave n-valeric, azelaic and succinic acids, indicating the following structure: CH₃•(CH₂)₃•CH:CH•(CH₂)₂CH:CH(CH₂)₇ COOH. Elseomargaric acid was reduced by the method Paal (Ber. 38, 1406 (1905)) when the method of Erdmann and Bedford (Ber. 42, 1324 (1909)) caused polymerization. The Na salt reduced better than did the acid. Wood oil acid, heated in No at 200-250°C. gave an oil of lower I no. and nn but the same sap. ño. This is probably not oxidation but anhydride formation. Elaeolic acid described by Cloez is probably a polymer of, and not an isomer of, wood oil acid. Polymerization takes place in 2 stages only by union of the double linkages in wood oil acids. In the 1st stage a soluble polymer is formed and in the second, a gel. In the polymerization of mixtures of wood oil and linseed oil, temperature and concentrations influence the rate but temperature alone determines the nature of the intermediate product.

Scheiber, J.

THE CONSTITUTION OF ELEOSTEARIC ACID.

Farbeu. Lack 1927, 646-7; C.A. 22, 2739 (1928).

"A brief review of the literature on the structure of eleostearic acid. S. agrees with Böeseken and Ravenswaay that there are 3 double bonds located in the 5,6-, 7,8- and 9,10-positions. Twenty-one references are given." From C. A.

Schneider, V. L., Holman, R.T., and Burr, G.O.

A MONOLAYER STUDY OF THE ISOMERISM OF UNSATURATED AND OXY FATTY ACIDS. J. Phys. & Colloid Chem. <u>53</u>, 1016-29 (1949)*; J. Am. Oil Chemists' Soc. <u>27</u>, 35 (1950).

"Force-area curves of monolayers have been studied and compared, using the following substances: stearic, oleic, linoleic, linolenic, arachidonic, elaidic, linolelaidic, elaidolinolenic, a- and β eleostearic, licanic, ricinoleic, ricinelaidic, 9,10-diketostearic, 9-keto-10-hydroxystearic, 9-hydroxy-10-ketostearic, and 9,10oxidostearic acids. With increasing numbers of double bonds per molecule, the limiting area increases in the naturally occurring unsaturated acid. Trans-isomers have smaller limiting areas than cis-isomers in the non-conjugated series. In the conjugated acids, trans isomers form condensed monolayers." From J. Am. Oil Chemists' Soc. (abridged)

a-Eleostearic acid is considered to have a cic-cis-cis configuration while β -eleostearic acid is the trans-trans isomer.

Shen, T.H., and Kuo, C.F.

A STUDY OF THE PROPERTIES OF ELEOSTEARIC ACID ESTERS FROM POLYHYDRIC ALCOHOLS.

Chiao-Tung Univ. Research Inst. Ann. Rept. Bur. Chem. <u>3</u>, 40-51 (1936); C.A. <u>31</u>, 3308 (1937).

"Pentaerythritol eleostearate is made by heating equimol. proportions of freshly prepd. a-eleostearic acid and pentaerythritol with 0.05-0.06 g. litharge as catalyst at 190° for 3.5 hrs. in a current of CO_2 . Mannitol eleostearate is prepd. in a similar manner, except that mannitol is used in place of pentaerythritol and the heating is carried out at 180° for 8.5 hrs. A synthetic resin is also prepd. by heating 112 g. tung oil 18.4 g. glycerol and 0.5 cc NaOEt to 250° for 1.5 hrs. in an oil-bath in a current of CO_2 , then cooling to 150°, adding 44.4 g. phthalic anhydride and reheating to 170° for 3/4 hr. in a current of CO_2 . The phys. and chem. consts. of this resin, as well as those of the 2 esters described above, were detd. Paints and varnishes were made from these 3 products. All 3 products are superior to tung oil in alk. test and dry more rapidly than tung oil." From C. A.

Steger, A., and Loon, J. van

THE POLYMERIZATION OF FATTY OILS. THE POLYMERIZATION OF ETHYL ELEOSTEARATE.

Fettchem. Umschau 43, 17-21 (1936); C. A. 30, 4022 (1936).

"Previous work (cf. C.A. 28, 5999; 29, 3536, 4190) on tung-cil polymerization was extended to include the heat polymerization of Et eleostearate (I), prepd. by esterifying eleostearic acid with EtOH and H_2SO_4 and distg. under vacuum. I was heated (a) to 280° and samples were taken at the end of 5, 10 and 15 min., (b) at various temps. for times required to cause gelation of tung oil, viz. 25 hrs. at 170° and 5 min. at 320° and (c) for 15 min. at 280° with addn. of 0.1% S. The polymerized prepns. so obtained were sapond., unsaponifiable material was removed, the acidic fatty residues were converted into the Et esters and distd. under high vacuum, 4 fractions being obtained from each prepn., viz. A b. up to 90°, B b. 90-100°, C b. 100-150° and D still residue. The consts. of the various fractions were detd. and tabulated. The small proportions of A obtained indicated that only small amts. of decompn. products were formed. Fractions B and D were hydrogenated at 140-150° and 40-50 atm. pressure with Pd on charcoal as catalyst. The amt. of H absorbed depended on the duration and conditions of hydrogenation. Thus, hydrogenation with colloidal Pd in alc. soln. at room temp. resulted in incomplete hydrogenation. The fatty acids in the thoroughly hydrogenated prepns. were sepd. into solid, semisolid and liquid fractions with the Pb salt method. The consts. of the various fractions are given and their properties discussed. Conclusions. Two reactions occur simultaneously when I is heated to high temps., (1) polymerization, i. e., formation of highly polymerized compds. by reactions between mols. of I and (2) rearrangement of I into a cyclic compd. (a sort of isomerism). Reaction 2 becomes more important above 300°. S acts as a pos catalyst for Reaction 2. Since the isomerate is incapable of polymerization, the effect of S being present is to prevent polymerization. Since polymerization of I does not cause its gelation, as with tung oil, heat treatment of I can be continued until the final product consists only of polymerizate and isomerate." From C. A.

Steger, A., and Loon, J. van

PO-YOAK, OIL.

Rec. trav. chim. <u>59</u>, 955-6 (1940) (in German); C.A. <u>35</u>, 4622 (1941). "Po-Yoak oil (I) obtained from the seed kernels of <u>Parinarium</u> <u>sherbronse</u> from Sierra Leone, consists mainly of the glycerides of eleostearic and coupeic acids. Carcful oxidation of Na soaps of the fat acids with alk. KMnO₄ gave dihydroxy- and tetrahydroxy-stearic acids showing the presence of 9,10-oleic and 9,10,12,13-linolic acids. From the thiocyanogen no. 76 it is concluded that no linolenic acid is present. Estm. of the diene no. 64 and carboxyl no. 78 establish the compn. of I as 41% coupeic acids, 31% eleostearic acids, 12% satd. material, 4.3% glycerols, 0.9 unsapond., 1.8% volatile and 8% linolic and oleic acids. This highly unsatd. oil is extremely liable to oxidation and polymerization." From C. A.

Steger, A., and Locn, J. van.

THE DIENE AND CAREONYL NUMBERS AND THEIR APPLICATION IN THE INVESTIGATION OF TECHNICALLY IMPORTANT PRODUCTS.

Fette u. Seifen <u>48</u>, 365-8 (1941)*; C.A. <u>37</u>, 543 (1943).

"Both the diene no. (I) and the carbonyl no. are useful in investigating fats of high mol. wt. which may replace china wood oil (II). Investigations of a synthetic oil "Synourin" made by dehydration of castor oil gave values of I varying between 15 and 23%. This shows that in "dienol" there is at most 26% glycerides of 9,11-linoleic acid, and not the 75% given by previous investigators. This throws doubt on the synthesis of "Trienol," the synthetic II. I of various equal viscosity II stand oils cooked at different temps. gave about the same I. Fat acids from II stand oil were converted to their Et esters and distd. into 3 fractions. The first two fractions contained esters of unchanged and cyclicized eleostearic acids as well as the satd. and unsatd. acids present in II. The distn. residue contained the polymerized material. Since the polymerizate had a I of 16.9 (polymerizates with a conjugated system should have a value of 45.7; their esters 41.5) the residue was a mixt. most of which did not have a conjugated system. Linseed-oil stand oil was converted to the ethyl esters and distd. It was not possible to det. from I whether conjugated bonds were formed by displacement of isolated double bonds. The authors found that by hydrogenation of II the I decreases regularly while the amt. of satd. acids remains practically unchanged. The hydrogenation is not selective with reference to the formation of 10,12-linoleic acid." From C. Α.

Steger, A., and Loon, J. van

FUNGU-OR BEHURADA OIL.

Fette u. Seifen 49, 769-70 (1942); C.A. 38, 1655 (1944).

"Fungu- or behurada oil is obtained from the seed of <u>Parinarium</u> <u>campestre</u>, a tree native of Surinam. The oil content of the kernel extd. with petroleum ether is 65%, but only 2.6% based on the wt. of the seed, because of the high percentage of husk. The oil cake consists of H_0O 2.2, ash 8.1, proteins 27.1, fibers and carbohydrates 62.2%; it contains some toxic matter and is not suitable for feed. The properties of the oil are: d_{70} 0.8874, n_{70}^{70} 1.4802, OH no. 26, I no. (Wijs) 132-138, sapon. no. 195.8, acid no. 2.3. The compn. of the oil is: unsaponifiable 0.3, glycerol residue 4.4, volatile and insol. 2.3, satd. acids 13.5, eleostearic acid 45.4, linolic acid 8.0 and oleic acid 26.1%. The low linolic acid content of this oil makes it unsuitable as a substitute for linseed or tung oils." From C. A.

ISOMERISATION OF POLYENE ACIDS AND CAROTENOIDS. PREPARATION OF BETA-ELAEOSTEARIC AND BETA-LICANIC ACID.

J. Am. Chem. Soc. <u>63</u>,3448-3452 (1941); Brit. Chem. Abstracts <u>1942</u>, A, II, 130.

"The isomerisation of oleic acid (I) and the readier isomerization of a-elaeostearic acid (II) and its esters by various reagents are described. That of (I) by NaNO₂ 30% HNO₂ and of (II) or a-licanic acid by a little I in MeOH has preparative val. Dihydroxyxanthophylls are converted by I into more strongly, and then (more I longer reaction) into less strongly, adsorbed pigments. Absence of OH decreases the ease of isomerisation. Esterification of OH also decreases the ease of change and leads to products which are separable by chromatography only after hydrolysis. Some adsorbents, e.g., synthetic, activated Mg silicate, although neutral in water, change carotenoids into blue substances similar to those obtained by strong acids or very strong bases. Care is thus needed in isolation of naturally occurring pigments, as accompanying acids may cause isomerisation; this may be avoided by adding org. bases, e.g., NPhMe₂, C₅H₅N." From Brit. Chem. Abstracts.

Sullmann, H.

ACTION OF LIPOXIDASE ON THE OXIDATION OF ELEOSTEARIC ACID. Helv. Chim. Acta 27, 789-93 (1944); C.A. <u>38</u>, 6301 (1944).

"It appeared of interest to study the behavior of lipoxidase (I) against a fatty acid with a conjugated unsatd. system such as eleostearic acid (II). Sumner has shown that the max. enzymic peroxidation of II in the presence of I is 16% of theoretical for 1 double bond, but only about 5% of the possible peroxidation on the basis of 3 double bonds. Manometric measurements of the consumption of 0 by suspensions of II at 37° in the presence of I from potato press juice and defatted soybeans, both in the active and inactivated state (inactivation by heating at 75-80° for 20 min.) and comparisons with similar measurements in the presence of hempseed ext. (free from I) indicate that the oxidation of II in the presence of I may be accelerated to a certain extent. The decided tendency of II to autoxidation makes more difficult the proof of the presence or absence of enzymic catalysis than in the study of the much less autoxidizable isomeric linolenic acid. Attempts to obtain conclusive evidence as to an enzymic oxidation of II in the presence of I by a preliminary study of secondary oxidation through the system I + II + acceptor (guaiacum resin or carotene) were futile. Decision as to whether II can serve as a substrate for I is accordingly postponed." From C. A.

Täufel, K., and Freimuth, U.

ACRCLEIN FORMATION FROM FATS.

Z. Lebensm. Untersuch. u. Forsch. <u>89</u>, 121-5 (1949); C.A. <u>43</u>, 5971 (1949).

"When fat was heated with KHSO,, the acrolein evolved from both free and bound glycerol. With eleostearic acid and tung oil which has been altered in light (oxidized) the glycerol radical is unimportant as the source of acrolein. That is, during oxidation

unsatd. acids are affected in some unknown manner so that they yield acrolein on heating. A parallel between this mechanism and that of conjugation does seem possible." From C. A. Thomas, A. W., and Thomson, J. C. PREPARATION OF PURE ELEOSTEARIC ACID FROM CHINESE WOOD OIL. J. Am. Chem. Soc. 56, 898 (1934); C.A. 28, 3051-2 (1934). "Details are given for the prepn. of a-eleostearic acid from tung oil and of the β-isomer from "wood oil butter." From C. A. Thorpe, J. F. ELAEOSTEARIC ACID. In Thorpe, J. F., and Whiteley, M. A. Thorpe's Dictionary of Applied Chemistry, Ed. 4, rev. and enl. London Longmons, 1940, W1. 4, p. 258. A brief review of the chemistry of eleosteoric acid. Toyana, Y., and Tsuchiya, T. NEW STEREOISOMERIDE OF ELAEOSTEARIC ACID IN POMEGRANATE SEED OIL. J. Soc. Chem. Ind. Japan 38, 182-5B (1935)*; Brit. Chem. Abstracts 1935, A, 960. "Punicic scid (I), m.p. 43.5-44°, has been obtained from the oil extracted by Et₂O from pomegranate seeds. When dissolved in light petroleum and kept during a week under CO_2 (but not H_2) (I) is converted into B-elaeostearic acid (II), m.p. 70.5-71°. (I) with Br in light petroleum affords a tetrabromide, m.p. 113.5-114°, identical with that obtained from (II). (I) is regarded as a stereoisomeride of (II) of the structure, Me [CH2]3. [CH:CH]3. [CH2]7. CO2H. This has been confirmed by ozonolysis of (I) and its Me ester." From Brit. Chem. Abstracts. Toyama, Y., and Tsuchiya, T. ANOTHER NEW STAREOISOMERIDE OF ELAEOSTEARIC ACID IN THE SEED OIL OF KARASU-URI, TRICHOS ANTHES CUCUMERCIDES. J. Soc. Chem. Ind. Japan 38, 185-7B (1935)*; Brit. Chem. Abstracts 1935, A, 960. "Trichosanic acid (I) m.p. 35-35.5°, has been isolated from the seed oil of karasuuri. In petroleum under CO2 or with a trace of I it passes readily into its isomeride, β -elaeostearic acid (II). (I) with Br in light petroleum affords a tetrabromide, m.p. 113-113.5°, identical with that obtained from (II)." From Brit. Chem. Abstracts. Toyama, Y. and Uozaki, K. LXPERIMENTAL RESULT OF THE REPEATED STUDIES ON THE PRESENCE OF OCTADECATRIENOIC ACIDS IN SEED OILS OF POMEGRANATE, KARASU-URI (TRICHOSANTHES CUCUMEROIDES) AND BALSAM PEAR. J. Soc. Chem. Ind., Japan 40, Suppl. binding 249-50 (1937)*; C.A. 31, 7684 (1937). "Punicic acid was reported as present in pomegranate seed oil and subsequently trichosanic acid was found in karasu-uri seed oil and also in balsam pear oil by Toyama and Tsuchiya. (C.A. 29, 5294; 30, 73721). In repeating the analysis at a later date, punicic acid

- 375 -

was again found in pomegranate seed oil, but no trichosanic acid was obtained from the seed oils of karasu-uri and balsam pear. A cryst. satd. acid was obtained from the former and an impure aeleostearic acid from the latter. This difference in results has not been accounted for thus far." From C. A.

Treibs, Wilkelm

AUTOXIDATION OF OXYGEN-ACTIVE ACIDS. VIII. INFLUENCE OF DILUTION. MONOMERIC 1 : 2- AND 1 : 4-ADDITION OF OXYGEN TO THE CONJUGATED DOUBLE LINKING SYSTEM OF ELAEOSTEARIC AND RICINENIC ESTERS. AUTOXI-DATIVE FISSION OF ACID CHAINS.

Ber. 76 (D, 670-5 (1943); Brit. Chem. Abstracts 1946, A, II, 121. "In the absence of a diluent, the addition of O₂ to Me elaeostearate exclusively causes dimerisation between pairs of ester chains oriented by intramol. forces with formation of perdioxan rings. With increasing dilution the cybotaxis of the mols. diminishes; therefore in increasing measure an O₂ mol. adds to an individual ester mol. without polymerisation, 1 : 2- and 1 : 4- addition occurring. The peroxidic 1 : 4-additive product isomerises to a dienil, converted by hydrogenation into the corresponding 1 : 4- glycol. The C chain of the monomeric, peroxide 1 : 2-additive product is divided into aldehydic fragments under the subsequent influence of catalysts. Autoxidation of Me ricinenate follows the same course.

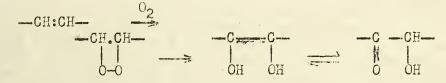
Autoxidation of Me elaeostearate in aq. COM2 containing an accelerator gives a peroxidic product which decomposes when distilled in a vac. giving appreciable amounts of volatile aldehydes and, mainly, Me azela-aldehydate [8-aldehydo-n-octoate] (I), b.p. 145-147°/20 mm. (semicarbazone, m.p. 107-108°). Hydrogenation of the autoxidised ester in presence of Pd-C followed by vac. distillation or fractional crystallisation leads to the following: lower aldehydes, (I), a glycol ester, C19H3804 (II), m.p. 65°, which is not a 1 : 2glycol [Pb(OAc)], small amounts of an incompletely examined ester, $C_{19}H_{36}O_4$, m.p. 30°, and a saturated compound, $C_{19}H_{32}O_8$, sol. in Na₂CO₃, containing 2 active H, which neutralises 2 equivs. of alkali in the cold and three in the hot and is doubtless a stable peroxide similar to that obtained by the autoxidation of Me linolenate under similar conditions. Formation of (I) is analogous to the ozonolysis of olefines but occurs only in particularly active systems of double linkings. Siccatives as autoxidation catalysts have a limited power of fission whereas reversible per-acids give (I) in 20% yield. (II) is also obtained from Me ricinenate; it can only be Me 9 : 12dihydroxystearate." From Brit. Chem. Abstracts.

Treibs, Wilhelm.

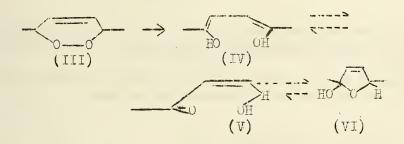
AUTOXIDATION OF OXYGEN-ACTIVE ACIDS. X. OXO-CYCLOTAUTOMERISM IN THE MONOMERIC AUTOXIDATION OF FLEOSTEARIC ESTER.

Chem. Ber. 80, 423-6 (1947); C.A. 42, 7707-8, (1948).

"It was shown in part VIII that the action of mol. O₂ on linolenic (I) and eleostearic ester (II) depends on the concn. Without diluent, 2 mols. O₂ add, with dimerization, to 2 ester chains, presumably forming perdioxane rings; diln. with an O-stable solvent (e.g. acetone), by hindering this cybotaxis (cluster formation), favors the formation of monomeric autoxidation products, by 1,2-addn., in part, of the O2. Toward a conjugated double-bond system, however, it partly assumes the role of an unsatd. philodienic component, with 1,4-addn. Hydrogenation of the 1,4-peroxides from I and II gives the same 1,4-diglycol, showing that the O2 adds at the same C atoms (9 and 12 ($_{\theta}$ and $_{\lambda}$)) in both I and II. From the different autoxidative behavior of the 2 classes of 0-active acids it had been concluded that only in conjugated systems are there intermolecularly active and directing forces which by the action of O produce polymols. through peroxide bridges. This conclusion is supported by the viscosity curve of mixts. in varying proportions of the 2 groups of esters with cyclohexane. While the viscosity curve of mixts. of cyclohexane with I (and also with linoleic and hexaenoic Me esters) almost coincides with the straight line running through the viscosities of the pure components, the curve for mixts. of cyclohexane with II falls steeply at first with increasing cyclohexane content and then tends to level off. The intermol. forces in the conjugated triene system which increase the viscosity by forming clusters act through a short distance and are rapidly rendered ineffective by diln. Peroxides formed by 1,2-addn. can rearrange and become stabilized as dienols and a-ketols:



It appeared possible that the 1,4-peroxides (III) formed in the autoxidation of I and II might rearrange into the dienols (IV) and HO ketones (V) and the latter tautomerize to 1,4-lactols (VI). This was confirmed by expt.



Me eleostearate (30 g.) in 300 cc. MeOH contg. 10 drops coned. M_2SO_4 , treated 24 hrs. at 40° with 0 introduced through a fritted glass distributor, yielded 80% of monomeric autoxidation product, m_D^{20} 1.4749, MeO 19.15%, which with H and a neutral Ni catalyst in MeOH at 60° and 70 atm. took up about 2 mols H per mol. ester in 1 hr.; fractionation of the product yielded: (1) 3 g. b₀ 60-125°, d_4^{20} 0.9600, reduces NH_3 -AgNO₃ (mirror) and Fehling soln.; (2) OHC(CH₂)₇CC₂Me, b₉ 125-45°, purified through the difficultly soluble NaHSO₃ compd. and characterized as the semicarbazone, m. 108° (3) a compd. (VII), $C_{20}H_{38}O_4$, by 220-30°, d_4^{20} 0.9735, n_D^{20} 1.4650, contg. 2 MeO groups (one of them saponifiable); and (4) a compd. (VIII), $C_{20}H_{38}O_5$, by 260-70°, d_4^{20} 1.0206, n_D^{20} 1.4722 contg. an acetylizable HO group. By analogy with previous experience, the primary 1,4-peroxide formation takes place at atoms 0 and λ , and VII is the lactol Me ether (IX, R= H). The free HO group in VII is probably on the furan nucleus (possibly IX, R = OH); as to the mechanism of its formation (perhaps from a 3,4-oxide), nothing definite can as yet be said. These expts.

CH₂ CHR (IX) He(CH₂)₅CH.0.C(OMe)(CH₂)₇CO₂Me

support the assumed oxo-cyclo (chain ring) tautomerism in the autoxidation of II in dil. soln. Under the same conditions, I, with 3 isolated double bonds, took up no appreciable amt. of O_{\bullet} " From C. A.

Ubbelohde, L., and Svance, T.

HARDENED OILS.

Seifensieder-Ztg. 46, 681 (1919); C. A. 14, 1228 (1919).

" * * *. Hydrogenation increases the sp. gr. and m.p. and decreases the I no. and n_D , but all 4 consts. retain a certain ratio to each other so that the simple detn. of the n_D will also give the other 3 values. In place of the m.p. the authors det. the dropping-point which in cottonseed, fish and wood oil is identical with the m.p. if above 40°, and 1-2 degree lower if below 40°; the dropping point of hardened linseed oil lies 1.0-1.5 higher than the m.p. if above 50° while in castor oil the 2 points are identical." From C. A.

Veen, H. van der

THE COMPOSITION OF LINSEED OIL.

Chem. Umschau Fette, Cole, Wachse u. Harze <u>38</u>, 277-9 (1931)*; C.A. <u>26</u>, 864-5 (1932).

The isomers of eleostearic acid are mentioned during the detailed discussion of the isomers of linseed oil acids.

Vercruysse, A.

THE CONSTITUTION OF ELECMARGARIC ACID.

Bull. soc. chim. Belg. <u>32</u>, 151-6 (1923); C.A. <u>17</u>, 2265 (1923). "Eleomargaric acid is known to contain 2 double bonds -- adding Br 4 atoms -- and 18 C atoms -- yielding stearic acid by hydrogenation. By oxidation with alk. KMnO₄ (103 g. KMnO₄ for 30 g. of the fatty acid) V. obtained valeric acid, identified as its Ag salt, and azelaic acid, identified by its m.p. and analysis. In this oxidation the larger part is oxidized to CO₂. The quantity of CO₂ formed agrees with the amt. calcd. By oxidizing with O₃ in CHCL₃ for 10 days, 50% valeric, 75% azelaic acid, and 9% succinic acid are obtained. V. concludes that eleomargaric acid has the structure Me(CH₂)₃CH: CH(CH₂)₂CH:CH(CH₂)₇CO₂H." From C. A.

Wan, S. W., and Chen, M. C.

PHYSIOCOCHEMICAL STUDIES OF ALPHA- AND BETA- ELEOSTEARIC ACIDS. I. MOLAR REFRACTIVITY AND PARACHOR.

J. Am. Chem. Soc. <u>61</u>, 2283-4 (1939); C.A. <u>33</u>, 8566 (1939). "Careful purification has given a-(I) and β -eleostearic acids (II) with the following properties: I, m.49-9.2°, d⁵⁰ 0.9028, q⁵⁰ 33.42, n⁵⁰ 1.5112, P 741 (calcd. 709), R (mol. refractivity 92.36 (calcd. 85.47); II, m. 71.5-2°, d⁷⁵ 0.8909 q⁷⁵ 31.04, n⁷⁵ 1.5022, P 736.9 (calcd. 709), R 92.20 (calcd. 85.47). While the difference in the found and calcd. values of P cannot be explained at present, the technique of the present procedure was checked with oleic acid with the following results: R 86.6 (calcd. 86.4), P 731.4 (calcd. 731.0)." From C. A.

Wheeler, D. H.

PROCRESS IN THE PROTECTIVE COATINGS AND PLASTICS INDUSTRIES. Ind. Eng. Chem. <u>41</u>, 252-8 (1949); C.A. <u>43</u>, 2787 (1949).

The reactions that occur during the drying of glycerides and other esters of unsaturated acids are reviewed with special attention to reaction mechanisms and functionality as introduced by Carothers. Thermal polymerization of methyl esters of unsaturated acids first causes dimerization, this reaction going fastest for conjugated acids such as those from tung oil. Methyl eleostearate has been assigned an average functionality between 1 and 2 because it thickens but does not gel. Glycol eleostearate forms an elastic, sticky gel when blown at 82°. Eleostearic acid, oxidized in amyl acetate solution, formed a dimer with 2 moles of oxygen per mole of original eleostearic acid. There appears to be a difference between the oxidative polymerization of conjugated and non-conjugated fatty esters. Conjugated oils, such as tung and oiticica, dry more rapidly and with less oxygen consumption.

Naterman, H. I., and Vlodrop, C. van.

TRANSFORMATIONS OF ESTERS OF UNSATURATED FATTY ACIDS WITH AND WITHOUT HYDROGENATION CATALYSTS IN THE ABSENCE OF HYDROGEN. J. Soc. Chem. Ind. 55, 320T(1936); C.A. 31, 1008 (1937). "Et eleostearate (I), Et lincleate (II) and Et cleate (III) have

been subjected to temps. of 180-200° without catalyst and in the presence of 5% Ni on guhr and 5% Pt on C. Tabulations of n_D^{20} , d_4^{20} , $(n^2 - 1)/d(n^2 + 2)$, and I no. are given to indicate changes. III is not transformed, I is changed only slightly, while II undergoes a marked transformation in the presence of the catalysts. Conclusion: Polymerization of II is preceded by mol. rearrangements producing a system which behaves like a conjugated system (cf. C.A. 24, 978)." From C. A.

Winter, G.

THE FROPERTIES OF MAKITA (KUSTA) OIL.

Australia, Dept. Munitions, Paint Notes 3, No. 12, 393-406 (1948)*; "Oil obtained in 18% yield from dried kernels of Makita or Kusta seed (from the tree <u>Farinair laurina</u>) had the following properties: sp. g. 50°/15° 0.939, n¹⁵= 1.5610, m. 38°, acid no. 11.8, sapon. no. 196, unsaponifiable matter 0.9%, Browne heat test 2-1/2 min. Absorption spectra measurements indicated the presence of 46% of parinaric acid and 34% of a conjugated trienoic acid, probably eleostearic acid. Varnishes made from the oil were superior to those of tung oil in drying time and water resistance. Catechol tannins (17.6%) were obtained from the dry oil-free kernels by water extn." From C. A. 43, 4031 (1949).

Woltemate, M. L., and Daubert, B. F.

HYDROGENATION OF METHYL BETA-ELEOSTEARATE.

J. Am. Chem. Soc. <u>72</u>, 1233-6 (1950); J. Am. Oil Chemists' Soc. <u>27</u>, 193 (1950).

"Data on the solvent hydrogenation of methyl β -eleostearate are reported. Trans-ll,l2-octadecenoic acid (vaccenic) was isolated from the products of hydrogenation and its structure and configuration confirmed." From J. Am. Oil Chemists' Soc.

VI. CAKE AND MEAL

Anonymous

PROBE USE OF TUNG MEAL AS INSECTICIDE.

Tung World 5 (3), 8 (July 1950).

It has been reported that finely ground tung meal is effective in repelling Mexican bean beetles, potato bugs, deer, rabbits and woodchucks from gardens.

American Society for Testing Materials.

REPORT OF SEED AND MEAL ANALYSIS COMMITTEE 1947-48.

J. Am. Oil Chemists' Soc. 25, 319-26 (1948); C.A. 42, 8495 (1948). "Eight subcommittees reported. The following made no recommendations because of incompleted work; Soy-flour sampling, soy-floursieving method, detn. of the water absorption of soy flour, development of a method for lecithin in soy flour, detn. of crude fiber in soy flour. The subcommittee for peanuts and peanut meal recommended that the tentative method (Ab-2-47) for the detn. of H_2O in peanut kernels be made official and also that the tentative method for the detn. of oil in peanut kernels be amended to specify the use of the Henry Nut Slicer instead of the Universal food chopper No. 1. The committee on tung fruit and meal analysis recommended that: (1) The method of sampling of tung fruit which has been studied by the committee be designated as a tentative method. (2) The method of analysis wherein the whole tung fruit is ground in a Wiley mill and subportions of the ground material are used in the H20 detn. and, after regrinding in a Bauer mill, used in the oil detn. be designated as a tentative method, with the use of a proper correction to be subtracted from the oil content obtained with the Wiley-Bauer ground fruit because of the extractable material from hulls and shells of the fruit which is not oil. (3) The method of analysis wherein the tung fruit is shelled and the H2O and oil are detd. on the kernel be designated as a tentative method. (4) Samples of tung fruit be sent out during the next season at least 6 times for analysis." From C. A.

Bryan, C. E.

DETOXIFICATION OF TUNG MEAL.

Tung World 4 (8), 8 (Dec., 1949).

A project was established at the Southern Research Institute to identify the toxic principle of the tung nut and to detoxify tung meal. The toxic component is an albumin. A secret process for detoxification renders the meal suitable for feeding poultry and cattle.

Davis, G. K., Mehrhof, N.R., and McKinney, R. S.

TUNG MEAL IN RATIONS FOR GROWING CHICKS.

Poultry Sci. 25, 74-9 (1945)*; C.A. 40, 3511 (1946). "The toxicity of tung meal prevents its use as a source of protein in poultry diets. At 10 and 15% levels, both the heat-treated and the raw meal caused high mortality in chicks, while at all levels above 5% feed utilization was greatly reduced. Toxicity was not destroyed by autoclaving at 22 lb. for 90 min. Exicity was also retained in heat-treated, 40-mesh screenings." From C. A.

Emmel, M. W.

THE TOXIC PRINCIPLE OF THE TUNG TREE.

Proc. Am. Tung Oil Assoc. 1945, 38-42; C.A. 39, 4165 (1945).

"The toxic principle considered indigenous to the tung tree is a saponin. Tests indicated its presence in the foliage, sap, and fruit. Oil-free tung kernels contain 7 to 8 times more saponin than an equiv. amt. of com. tung meal. Feeding expts. with young chicks indicate that com. tung meal contains a 2nd toxic substance which is partially destroyed by heat or hydrolysis. Fresh tung meals contain this 2nd toxic substance in greater quantity than old meals. Expts. are now in progress to det. the origin of the 2nd toxic substance." From C. A.

Emmel, M. W.

TOXIC PRINCIPLE OF THE SPECIES OF ALEURITES.

J. Am. Vet. Med. Assoc. <u>111</u>, 386-7 (1947)*; C.A. <u>42</u>, 2367 (1948). "Besides saponin a second toxic fraction was identified in tung meal. Com. tung meal could be detoxified by extn. with hot 95% EtOH to remove the second toxic principle and by acid hydrolysis to remove the saponin." From C. A.

Erickson, J.L.E., and Brown, J.H., Jr.

TOXIC PROPERTIES OF TUNG NUTS.

J. Pharmacol. 74, 114-17 (1942)*; C.A. 36, 2328 (1942).

"The toxic principle of tung nuts is not present in tung oil but is found in tung meal. It is destroyed by prolonged heating at 70-100°, or by steaming 2 hrs. under pressure. Attempts to isolate the toxic substance failed." From C. A.

Godden, W.

THE FEEDING VALUE OF TUNG-SEED MEAL.

Bull. Imp. Inst. <u>31</u>, 352-8 (1933); C.A. <u>28</u>, 1421 (1934). "Tung-oil cake and extd. meal are fairly rich in protein and carbohydrates. The meal contains some substance which makes it unpalatable and some irritant material which has a harmful effect on the mucous membranes of the intestine." From C. A.

Henry, T.A., and Auld, S.J.M.

THE OCCURRENCE OF CYANCGENETIC GLUCOSIDES IN FEEDING-STUFFS. J. Soc. Chem. Ind. 27, 428-33 (1908).

In the discussion following the main paper Dr. Diver mentioned the belief in Japan that the press cake left from the expression of China wood oil is poisonous and useful only as manure. A Japanese pharmacologist found the cake not poisonous to animals. The authors believed the poison to be HCN and proposed to search for it in the uncooked China wood plant. McKinney, R. S.

MISCELLANEOUS STUDIES AT THE GAINESVILLE TUNG-OIL LABORATORY. Proc. 10th Ann. Convention, Am. Tung Oil Assoc. and United Tung Growers Assoc. 1944, 59-63; C.A. <u>39</u>, 2890 (1945).

"Tests indicate the possibility of prepg. a moldable plastic from solvent-extd. tung meal. Solvent-extd. tung meal and press cake with and without autoclaving for 2 hrs. with steam at 25 lb. pressure were used in feeding tests with chickens. The materials not autoclaved were definitely toxic. With autoclaved tung-oil press cake in the diet up to 30% the chickens did not lose weight but they looked unhealthy. A new clarification process for crude tung oil is suggested in which sodium bisulfite is used to ppt. the nonoil constituents. Tests showed the new process to be better in certain respects than the diatomaceous earth filter aid now used in the tung-oil mills." From C. Å.

Pollard, C.B., and Ellis, L.M.

THE DETERMINATION OF THE TUNG OIL IN MEAL AND PRESS CAKE. Am. J. Pharm. 108, 31-2 (1936); C.A. 30, 2778 (1936).

"A Soxhlet app. with a thimble of about 50 cc. capacity was used. The tared 250-cc. flask was attached by a 2-hole cork carrying an inlet tube through which an inert gas was passed to keep the O swept out of the app. Since the current of gas passing through the app. tends to cause unduly rapid evapn. of the solvent used, an aspirator bottle contg. solvent was introduced into the gas line. CCl, was used as the solvent and N as the inert gas. The samples were kept in an atm. of N in sealed cans prior to the extns. Rapid handling was necessary in all operations where the material was exposed to the air. In carrying out the detn. on the press cake, a suitable quantity was crushed in a large mortar, and a 25 to 40-g. sample accurately weighed in a watch glass. This was transferred to the Soxhlet thimble and placed in the app., the app. swept out with a slow stream of N, and the extn. carried on for about 10 hrs. A very slow stream of N was passed through the app. throughout the time of extn. At the end of this time the Soxhlet flask was removed, the solvent evapd. off on a steam bath with a stream of N passing into the flask to hasten evapn. and prevent access of 0 and the flask and residue weighed. The meal was sifted through a 14-mesh sieve before extn. in order to remove trash and large pieces of the meal. Approx. 10-g. samples were used, and the extn. was carried on over a 24-hr. period. Shorter time gave results indicating incomplete extn. Otherwise the procedure was the same as for press cake. The following percentages of tung oil were obtained: press cake, samples A 4.79 and 4.83, B 4.94 and 4.79, C 6.01 and 6.00, D 4.65 and 4.62; meal, sample E 48.61, 47.98 and 48.56." From C.A.

Rusoff, L.L., Mehrhof, N.R., and McKinney, R.S.

CHICK FEEDING EXPERIMENTS WITH SOLVENT-EXTRACTED TUNG-OIL MEAL. Poultry Sci. 21, 451-4 (1942)*; C.A. 36, 7173 (1942).

"Exptl. results of feeding solvent-extd. tung-oil meal to growing chicks at levels of about 5-20% of the ration indicated that it was unpalatable, but there was no definite evidence of toxicity. Com. tung-oil meal is toxic and should not be used for feeding purposes." From C. A. Taggert, W. G.

RESEARCH IN AGRICULTURE.

Louisiana Agr. Expt. Sta., Ann. Rept. 1944-45,9-10 (1946); C. A. <u>41</u>. 1791-2 (1947).

Contains summaries of research studies including the following: detoxification of tung meal; toxic principles of the tung nuts.

Taggert, W. G., & Forbes, I. L.

RESEARCH IN AGRICULTURE.

La. Agr. Expt. Sta. Ann. Rept. <u>1945-46</u>, 8 (1947)*; C. A. <u>41</u>, 7598 (1947).

Results of experimental studies are reported including one on the toxic principles of the tung nut.

Yeh, H. L.

PROTEINS OF TUNG NUT.

Thesis, Ph.D., Univ. of Michigan, 1945, 186 pp., Michigan Univ. University Microfilms Pub. no. 704; Microfilm Abstracts 6 (2), 14-15 (1945).

"An albumin (N 14.3 S 0.79%) and a globulin fraction (N 17.5, S 1.75%) have been isolated from the defatted meal and the aminoacid constitution was examined. The digestibilities in vitro (73.4 and 82.4%) were lower than those of many seed globulins." From Brit. Chem. Abstracts 1947, A, III, 288. VII. PRODUCTION, TRADE STATISTICS, ECONOMICS

Anonymous

CHINA WOOD OIL MARKET UNSETTLED BY ORIENTAL POLITICS.

Paint, Oil Chem. Rev. 83 (1), 13 (Jan. 6, 1927).

The demand for tung oil is strong but the supply that will be available in the near future is uncertain because of political uncertainties in China. The current price (tank cars) is 10.5 cents per 1b.

Anonymous

CHINA WOOD (TUNG) OIL TRADE.

Inspection and Commerce J. (China) 6 (8), 6-8 (1935).

The quantities of wood oil exported from China are tabulated for each year from 1912 to 1934. For 1934 the quantities shipped from each of 17 Chinese ports and the quantities received by 12 importing countries are also tabulated.

Chinese exporters, profits and grades of tung oil are included.

Anonymous

POST-WAR COMMODITIES. I. TUNG OIL.

Statist. 140 (3384), 8-9 (Jan. 2, 1943)*; Bibliog. of Agr. 2, A, 171, (1943).

"Notes on the possible post-war expansion of the use of tung oil mainly in connection with building activities, and its possible development for making waterproofed paper." From Bibliog. of Agr.

Anonymous

THE FUTURE OF TUNG OIL; POSSIBILITIES OF LARGE-SCALE AFRICAN PRODUCTION. African World 142, 203 (Mar. 27, 1943)*; Bibliog. of Agr. 3, K, 32 (1943).

Anonymous

JONES HAILS SOUTH'S TUNG INDUSTRY.

Tung World 1 (2), 4 (May, 1946).

Excerpts from an address by S. H. Jones, former Governer of Louisiana, on the economic opportunities of the tung industry.

inonymous

OITICIC. NOT A SUBSTITUTE FOR TUNG OIL, SAYS EXPERT. DR. CRANE TRACES HISTORY OF NEWLY DEVELOPED PRODUCT FROM BRAZIL. Tung World 1 (11), 6 (Mar., 1947).

Oiticica oil is not equivalent to tung oil but is intermediate in quality between tung oil and linseed oil.

Anonymous

TUNG FRUIT FRODUCTION FOR U. S. Tung World 2 (9), 15, 22 (Jan., 1948). Tung fruit production in air-dried tons: 1944, 26,680; 1945, 37,080; 1946, 57,400; 1947, 66,700.

Ancnymous

TUNG OIL. PAST, PRESENT AND FUTURE.

Proc. Am. Tung Oil Assoc. 1948, 44-56.

A review of the uses of tung oils in protective coatings with special attention to economic factors governing the selection of tung oil or a substitute.

Anonymous

TUNG CIL SHIFMENTS FROM HONG KONG.

Chem. Eng. News 27, 2501 (1949).

Exports from Hong Kong, Jan. 1 - May 1, were 19,100,000 lbs., of which U. S. received 1,100,000 lbs. During the same period of 1948 U. S. received 11,000,000 of a total of 20,500,000.

Anonymous

EFFECT OF CONJUGATION OF ISCLATED DOUBLE BONDS ON THE DESICCATION OF VEGETAELE AND MARINE OILS.

Chem. Obzor 24, 18-20 (1949)*; C. A. 43, 5609 (1949).

"If double isolated bonds are changed into the double conjugated bonds, linseed oil acquires the desirable characteristics similar to that of tung wood oil for paint and lacquer manufacture. The conjugation is desirable only to certain degree (50%) and it is carried out at normal pressure, 180 to 200° and with the addition of Ni catalyst contg. S for 15 to 45 min." From C. A.

Anonymous

SUPPORT FRICE BOOSTED TO 25.1 CTS.

Tung World 5 (6), 4 (Oct. 1950).

"Growers guaranteed \$63 per ton for 17.5 pct. nuts; Loan Program at 3 pct. Also approved; 20 carloads of Oil Tendered CCC." Subtitle.

Anonymous

STATE DEFT. VOIDS CHINA OIL PACT.

Tung World 5 (4), 4 (Aug. 1950).

"Way Cleared for Tariff As CCC's Washington Officials Hold Session With Growers, Millors" Subtitle.

Bailey, A. E.

THE NEW CHEMISTRY AND TECHNOLOGY OF OILS AND FATS.

Chrenica Botan. 2, 128-35 (1945); C. A. 40, 2655 (1946).

"A general discussion of the occurrence of oils and fats, utilization of fats, the compn. and structure of natural fats, the preservation of edible fats, fractionation of fatty materials, polymerized oil products, and the surface activity of fat derivs. [Tung oil is especially prized because of its conjugated double bonds which give it an exceptional ability to polymerize. The shorteges of tung oil caused by the war have led to extensive production of conjugated drying eils by the dehydration of castor oil and by the alkali isomerization of non-conjugated eils like linseed.] 53 references." From C.A. Behr, O. M.

MANUFACTURED DRYING OILS

Official Digost Federation Paint & Varnish Production Clubs No. 195, 203-11 (1940); C. A. 35, 3836 (1941).

"China wood oil (I) may be replaced by oiticica oil (II), dohydrated castor oil (III) glycerides of fractionally distd. fat acids (IV) (from fish oil), and segregated oils (V) (natural oils from which the nondrying constitutents havo been partly removed). Films from II tend to check on aging; those from III are soft and slow-drying; IV sets up fast but remains tacky. V in partly polymerized form (Polymerol A) is faster drying and more waterproof than polymerized I, does not frost and has good resistance to actinic light. V has a very low acid no. and is stable toward ZnO. It is compatible with the common resins but, with the phenolic and alkyd resins, equal wts. of resin and oil should first be blended hot, then further mixed with more oil." From C. A.

Brandt, K.

ECONOMIC ASPECTS OF FATS AND OILS IN 1940 Official Digest Federation Paint & Varnish Production Clubs No. 200, 431-9 (1940); C. A. 35, 3111 (1941) (No Abstract). Prices and production of many oils are surveyed. Because of the high price (\$0.26 per 1b.) of tung oil the author anticipates that less expensive substitutes will be developed.

Brannt, W. T.

WOOD OIL OR TUNG OIL
In Animal & Vegetable Fats and Oils, H. C. Baird and Co., Phila.,
Pa., 1896, Vol. 2, p. 4.
A brief review.

BUSER, K.

USE OF DOMESTIC (GERMAN) RAW MATERIALS IN THE PAINT INDUSTRY.
Farben-Ztg. 39, 1240-1, 1263-5 (1934); C. A. 29, 1267 (1935).
"Tung oil is the most important foreign raw material for paints.
B. discusses the possibility of replacing it with linseed oil, nitrocellulose lacquer, chlorinated rubber, alkyds, chemically changed fatty oils, etc." From C. A.

Carabia, J. P.

NATURAL PRODUCTS AND AGRICULTURE IN PARAGUAY. In Plants and Plant Science in Latin America, Franz Verdoorn, ed. Chrónica Botànica Co., Waltham, Mass., 1945, pp. 125-127; Biol. Abštracts 20, 863, Abs. No. 7883 (1946).

"A review of the usoful plants of Paraguay under the following headings: Cattle raising, cotton, quebracho, lumber in general, yerba mate, small grains, tobacco, sugar cano, rice, tung oil, etc." From Biol. Abstracts. Catton, David S. RAW-MATERIAL SURVEY. Can. Paint & Varnish Mag. 23 (1) 6, 8, 10, 12, 43-5 (1949); C. A. 43, 2787 (1949). "A survey of raw materials in the Canadian paint and protective coatings industry in the latter half of 1948." From C. A. Tung oil mentioned as being uncertain in supply because of the Chinese political situation and the expectation that none of the U. S. production will be exported. The price of U. S. tung oil is 23-1/4¢ per 1b. China Bureau of Public Information. Shanghai THE GREAT CHINESE WOOD-OIL INDUSTRY. Millard's Rev. 10, 163-8 (1919); C. A. 14, 850 (1920). "A comprehensive review of the extent of the China-wood-oil trade. Methods for increasing the production and improving the quality are indicated." From C. A. Chopp, C. C. REMARKS [TUNG OIL PRICE FLUCTUATIONS] Proc. Am. Tung Oil Assoc. 1946, Pt. I, 27-9. A discussion of the price fluctuations experienced by tung oil in the past. Highly fluctuating markets are undesirable. Concennon, C. C. TUNG OIL. ITS PRODUCTION AND COMMERCIAL VALUE. Am. Paint J. 21, 54-8 (April 26, 1937); C. A. 31, 4513 (1937). "A discussion of the American tung-oil industry." From C. A. Concannon, C. C. TUNG OIL BELT IS TIGHTENED. U. S. Dopt. Com. Domestic Commerce 31 (17), 32-4 (April 29, 1943)*; Bibliog. of Agr. 3, K, 32 (1943). "Growth of tung oil production in the United States from 1932 to 1942, and prospects for 1943." From Biblicg. of Agr. Crantham, H. G. ADDRESS [ACCOUNTING IN THE TUNG OIL INDUSTRY] Pros. Am. Tung Oil Assoc. 1948, 40-3. A discussion of accounting as it pertains to the tung industry. Darwin, Joseph TUNG IN THE ECONOMIC DEVELOPMENT OF LOUISIANA. Proc. Am. Tung Oil Assoc. 19/4, 70-3. Plans are mentioned for increasing the acreage of tung orchards from 27,900 in 1944 to 125,000-135,000 in 1954.

Dean, J. M.

TUNG OIL INDUSTRY IN MISSISSIPPI AND FUTURE OUTLOOK.

Proc. Am. Tung Oil Assoc. 1944, 83-6.

A brief review. Temperature and rainfall in Southern Mississippi are like those of the tung producing areas of China. Tung production in Southern Mississippi is profitable when proper fertilization and cultivation are practiced. The crop has reached an annual value of \$1,000,000 based on the current price of \$0.39 per lb. for the oil. Post-war expansion of the tung industry may be delayed due to unusually large demands for food products.

DeLong, G. C.

THE USES AND PRODUCTION OF TUNG OIL.

J. Goog. (Lancaster) 41 (8), 309-12 (1942)*; Biol. Abstracts 17, 1555, Abs. No. 17,204 (1943).

"Tung oil, the fastest drying oil, becamo known in the U. S. during World War I. Although indigeneous to parts of Malaya, Africa, and some Pacific Islands, China is the chief producer and exporter. Sensitive to cold weather Aleurites fordii, the chief species, is raised in central China and A. montana in tropical Kwangsi Province. Seeds introduced into U. S. in 1905 were planted in Ala., Fla., La., Miss., So. Car., and Tex. The Bureaus of Chemistry and Soils and of Plant Industry, aided by state and local agencies, have assisted with the expts. Although producing only a neglible amount of oil at present, the number of trees in the U. S. is increasing and some authorities think the U. S. can provide for its own needs by 1947. The quality of the Am. oil is higher than the Chinese." From Biol. Abstracts.

DeLong, G. C.

THE USES AND PRODUCTION OF TUNG OIL. Trans. Illinois State Acad. Sci. 35 (2), 121-3 (1942)*; Bibliog. of Agr. 2, A, 290 (1943).

Eisenschiml, Gerald

DRYING OILS, THEIR PRESENT STATUS AND FUTURE PROSPECTS. Paint Varnish Production Mgr. 21, 66-72 (1941); Am. Paint J. 25, 7-9, 64, 66, 68, 70, 72 (Feb. 17, 1941); Paint, Oil Chem. Rev. 103 (6), 18, 49; (8), 32-3 (1941); C. A. 35, 2735-6 (1941). "A discussion of the sources and uses of (1) soybean oil (a semidrying oil), (2) menhaden and sardine oils, (3) linseed oil, (4) dehydrated castor oil, (5) perilla oil, (6) oiticica oil and (7) China wood oil." From C. A.

Eisenschiml, Otto, and Eisenschiml, Gerald.

REVIEW OF VEGETABLE OIL TRADE IN LAST QUARTER, 1941.
Am. Paint J. 26, 7-9 (Jan. 5, 1942)*; C. A. 36, 1506 (1942).
"The oconomic status of tung, oiticica, dehydrated castor,
linseed and sardine oils and turpentine is indicated." From C. A.

Eisenschiml, Otto, and Eisenschiml, Gerald. POSTWAR PROSPECTS FOR DAYING OILS. Chem. Eng. News 23, 33-6, 85 (1945); C. A. <u>39</u>, 1549 (1945). (no abstract). Linseed, tung, and oiticica are singled out. Fetrow, W. W., and McVey, D. H. A LONE EAGLE-OZONE TUNG CO-OP. News Farmer Coops. 16 (2), 5, 18-19 (May, 1949)* Fehr, Frank & Company. ANNUAL REVIEW FOR 1947 OF OILSEEDS, OILS, OILCAKES AND OTHER COMMODITIES. Fehr & Co., London, 1948, pp. 21, 24, 26, 27, 31. Exports from China (tons of 2,240 lb.) 80,537 (1947); 35,264 (1946).Imports into U. K. (tons) 7,639 (1938); 355 (1945); 3,992 (1946); 8,707 (1947). Imports into U. S. (tons) 790 (1945); 16,161 (1946); 54,270 (1947). Imports into France (tons of 1000 Kg) 146 (1939); 1,513 (1947). Imports into Sweden (tons of 1000 Kg) 915 (1946); 2,742 (1947). Gardner, H. A. TRADING RULES ON TUNG OIL. Am. Paint, Varnish Mfrs. Assoc. Circ. 335, 619 (1928); C. A. 22, 3998 (1928). Rules presented in Circular 326 were approved by the Educational Bureau with a suggestion for their use on trial for six months. Gardner, H. A. DRYING OILS FOR THE INDUSTRY. Am. Paint J. 22, Convention Daily 7-8 (Oct. 30, 1937)*; Paint, Oil Chem. Rev. 99, (23), 134-5*; Oil, Paint Drug Reptr. 132, (19), 47-8, 50 (1937)*; C. A. 32, 811 (1938). "The shortage of tung oil has resulted in the development of substitutes. Among these are the alkyd. synthetic resins, Cashew .nut oil, Chia: oil, hempseed oil, Jap wood oil, lumbang." From C. A. Gardner, H. A. THE DRYING-OIL SITUATION IN AMERICA. News Ed. (Am. Chem. Soc.) 18, 358 (1940); C. A. 34, 4593 (1940). "Unsettled political situations in the Far East result in periodic dislocations in the supply of tung oil, which normally contributes about 20% of the oils used in the paint and varnish industry. By tables and charts the imports and factory consumption of oils are shown. It is suggested that greater efforts be made to produce synthetically oils for industry rather than to depend upon greater growing capacity. Chlorination of nondrying oils and subsequent dechlorination, with the production of unsatn., may ultimately be developed along practical lines." From C. A.

- 390 -

Gay, E. C.

PRESIDENT'S ANNUAL REPORT.

Proc. Am. Tung Oil Assoc. 1948, 7-10.

Over 130,000,000 lbs. of Chinese wood oil was dumped on American markets in 1947 causing the members of the American Tung Oil Association to seek a tariff on imported wood oil. A bond of \$0.025 per lb. has been placed on imported Chinese oil.

Groggins, P. H.

GLYCERIDIC OILS IN OUR NATIONAL ECONOMY.

J. Am. Oil Chemists' Soc. 26, 356-9 (1949); C. A. 43, 6841 (1949). Domestic production of tung oil, 17-18,000,000 Ibs. per yr., could take care of only our most critical needs in an emergency.

Ho, K.

TUNG OIL OF KWANGSI PROVINCE, PLANTATION, PRODUCTION, TRANSPORTATION, TRADE, ETC.

Chinese Inst. Engrs. Special Kwangsi Investigation Rept., 1936 (in Chinese)

How, Bang

CHINESE-AMERICAN TUNG PROBLEMS OF MUTUAL INTEREST.

Proc. Am. Tung Oil Assoc. 1944, 77-82.

Importers of Chineso wood oil and producers of American tung oil have a common interest in protecting the markets which they jointly supply. Since American production is insufficient to supply American markets imports are necessary. Fears that Chinese oil will flood American markets are unfounded because there have been developed in China new uses for tung oil as fuel for lamps and for the production of gasoline. The history of tung is reviewed from its first known mention in connection with paints in the "Book of Poetry" edited by Confucius over 24 centuries ago up to the present. Imports into the U. S. were as follows: First recorded shipment, 1869, value \$62; 1869-1870, 381,000 lbs.; 1883-1884, 1,000,000 lbs.; 1910-1911, 53,000,000 lbs.; 1928, 107,000,000 lbs.; 1937, 175,000,000 lbs. The Universal Trading Corp. was founded in 1938 for marketing Chinese wood oil in the United States and for purchasing American manufactured goods.

Ivanova, A. A., and Bespalko, A. I. TKEATING CASTOR OIL FOR THE PURPOSE OF OBTAINING A TUNG-OIL-TYPE PRODUCT. Khim. Prom. 1945 (12), 11-14; C. A. 40, 5264 (1946). "Dehydration of castor oil in the presence of several catalysts was studied. The purpose was to produce a drying oil of the tungoil type." From C. A. (abridged).

Jackson, D., and Eiland, J. C. TUNG. OLD CLOP WITH NEW USES. Am. Paint J. 33 (38), 66-7, 70, 72, 74, 77 (June 13, 1949); For Salo, Want and Exch. Bull. (Fla. State Mktg. Bur.) 12 (2), 1 (May 2, 1949).

Jones, S. H.

ADDRESS [THE SOUTH'S ECONOMICS]

Proc. Am. Tung Oil Assoc. 1946, Pt. 1, 18-26.

Refers to the tung industry as "one of the bright spots on the future economic horizon of the South."

Kester, E. B.

MINOR OIL-PRODUCING CROPS OF THE UNITED STATES.

J. Am. Oil Chemists' Soc. 26, 65-83 (1949).

Tung oil and tung fruit are included in an extensive list of cils and cil-bearing plant products grown in the U.S. 9 tung references.

Lagasso, F. S.

THE PLESENT STATUS OF THE DOMESTIC TUNG INDUSTRY. Froc. Florida Acad. Sci. 7 (2/3), 133-7 (19/4)*; Biol. Abstracts

20, 800, Abs. No. 7288 (1946). "The tung tree, Aleurites fordii, was introduced into the U. S. from China in 1904. In 1944 the value of the annual crop was roughly 2 million dollars and it was increasing rapidly. During the war the growing of tung oil became a highly profitable industry, but such high prices will probably not be permanent." From Biol. Abstracts.

Le Peau, N. X.

THEAE IS NO 100 FCT. TUNG SUBSTITUTE. Tung World 1 (1), 12 (1946).

All so-called tung oil substitutes are inferior to tung oil in one or more properties.

Li, Ying-Chen

CHINA NOW HAS 1,742,000 ACRES FLANTED IN TUNG TREES, STUDY SHOWS. Tung World 1, (9), 6-9, 18 (Jan., 1947).

Excerpts from "A Comparative Study of Seed-Production of Several Varieties of Alcurites fordii Hemsley, The Chinese Tung Oil Tree, on the basis of Quantity, Quality and Oil-Producing Ability" discuss acreages and varieties of the tung tree in China.

Liu, H.

THE TUNG OIL INDUSTRY. China Min. Agr. and Forestry, Misc. Fub. 1, 52-5 (April, 1948)*

Lun, Y. P.

TROBLEMS OF IMPROVING THE OUTFUT AND MARKETING OF TUNG OIL. Monthly Farmers' Bank China 9 (5), 34-7 (May 1948) (in Chinese)*

LYTTON, H. D.

THE 1937 CONSUMPTION OF TUNG OIL.

Am. Faint J. 23, 21-3, 26, 28 (Nov. 28, 1938)*; C. A. 33, 1161 (1939).

An interpretation of the statistics on consumption of tung oil.

McCandliss, D. A.

HOW AND WHY THE GOVELNMENT TUNG NUT ESTIMATES ANE PREPARED.

Proc. Am. Tung Oil Assoc. 1944, 103-5.

Voluntary reports by farmers, millers, warehousemen, etc. are analysed for the benefit of producers and consumers.

McDaniel, J. A., and Stanley, F. E.

AN ECONOMIC AMALYSIS OF THE TUNG INDUSTRY IN LOUISIANA.

Louisiana Agr. Expt. Sta., Mimeograph Circ. 119, 39 pp. (Doc. 1950). "---a survey of tung nut farms was made during the summer of 1949. Data relating to the 1948 crop were collected and analyzed. The study was planned with the following major objectives: (1) to determine cultural requirements and practices for the successful production of tung nuts on a commercial scale; (2) to develop input requirements for establishing a commercial tung erchard; (3) to determine costs and returns from the tung enterprise; and (4) to summarize existing marketing methods and practices." From the Introduction, p. 1.

"1. Tung nut production is a relatively new farm enterprise in Louisiana, and has become of commercial importance in the state since 1940."

"2. Tung was the major crop on all farms surveyed."

"3. All forms surveyed were highly mechanized."

"4. Tung is different from the annual crops in that a crop of nuts of commercial importance is not produced until about the fourth year. Therefore, orchard development is a long time investment. Approximately 36.7 hours and 10.5 tractor hours are required to establish and develop one acre of trees."

"5. The cost of establishing and developing an acre of tung for three years was \$65.94 at 1948 prices, \$47.03 at 1943 prices and \$36.23 at 1939 prices."

"6. Iroduction and harvesting practices varied considerably. However, the most common practices were to cultivate twice, fertilize once or twice, cut briars and sprouts once, harvest the nuts by going over the orchard twice, place the nuts in sacks hung in trees to air dry, and haul the nuts from the field to the mill."

"7. The cost of growing and harvesting an acre of tung under 1948 conditions was \$34.97, when yields of 1,100 pounds per acre were obtained."

"8. The cost of producing a ton of nuts varied inversely with the yield of nuts per acre."

"9. Two methods of farm storage wore reported: (1) as nuts were harvested, they wore sacked and hung in trees to air dry; and (2) after the nuts were harvested, they were loaded on wagons and hauled to specially-built, ventilated sheds to dry."

"10. Roducing the amount of man labor required per acre seems to be one of the best opportunities of cutting costs for tung farmers."

"11. The cattle onterprise is well adapted to a farm organization built around tung nuts as the major cash crop." Selections from the Summary and Conclusions. pp. 37-39. Markley, K. S.

FAT AND OIL RESCURCES OF LATIN AMERICA

In Plants and Plant Science in Latin America, Franz Verdoorn, ed. Chronica Botánica Có., Waltham, Mass., 1945, pp. 211-218; Oil Mill Gaz. 51, (6) 9, 11, 23-30 (1946); C. A. 41, 4319 (1947); Biol. Abstracts 20, 193, Abs. No. 1644 (1946).

"Distribution, economics, importance, and uses of the following South American oils are briefly discussed: babassu, coconut, cohune, noli, corozo, dende palm, oiticica, Garcia nutans, garampara, cocoa, ucuuba, castor, linseed, tung, sunflower, cottonseed, peanut, and a miscellaneous group." From C. A.

Martin, W.

INCREASE IN WOOD OIL TRADE.

Daily Consular and Trade Reports, (U. S. Dept. Com. and Labor), No. 2889, pp. 2-3 (June 7, 1907).

Wood oil exports from Hankow, China, to the U. S. were 48,203,067 lbs. (\$337,234) in 1905 and 58,550,933 lbs. (\$720,598) in 1906.

Melling, E.

TUNG-OIL SUBSTITUTION.

Paint Manuf. 9, 347-50 (1939); C. A. 34, 1199 (1940).

"There are 3 main types of substitution, either partly or wholly as follows: (1) by resin or resin mixts., (2) by other oils, (3) by other materials, as chlorinated rubber. The type of substitute is dependent upon the outstanding property required of the finished product. In retaining drying speed resin substitute is suitable, but at the expense of flexibility, outside life and like characteristics. Combinations such as 100% phenolic resins and linseed oil, alkyd resin plus linseed oil-copal ester varnishes, the substitution of perilla, oiticica, dehydrated castor and fish oils for tung oil are discussed. None of these completely fulfills the properties of tung oil. It is necessary to formulate the medium for the particular job, not the primary characteristics wanted and formulate accordingly using mixts. of oils and resins till the most satisfactory product is found. Chlorinated rubber may replace the tung oil-100%

Merz, C.

PROGRESS IN THE FIELD OF OIL-ECONOMIZING AND OIL-FREE PAINTS. Chem. Fabrik 1938, 568-74*; C. A. 33, 2352 (1939).

"Imports of flaxseed and of linseed, castor, wood, whale, fish, seal and oiticica oils for 1932-7 are tabulated. Work on the partial or complete substitution of the usual oils by varnishes, refined train oil, "TallUl" (liquid resins from the manuf. of cellulose from pine), alkyd resins alone and combined with nitrocellulose is reviewed. The approx. compn. of some of the mixts. and the oil savings are tabulated and some applications of the paints are given and the results discussed and illustrated. The oil-free coatings discussed are chlorinated rubber, color lacquers, and lacquers of nitrocellulose, synthetic rosins and benzylcellulose, with the percentages of oil saving indicated. Eight references." From C. A.

Moffitt, R. M.

SUPPLEMENTARY USES OF TUNG LAND.

Proc. Am. Tung Oil Assoc. 1942, 17-20.

. Portions of a tung farm which were unsuited to the growth of tung trees were profitably used for raising cattle and growing pecans.

Moldenko, H. N.

VITAL VEGETABLE OILS.

Nat. Hist. (New York) 53 (5), 231-7 (1944)*; Biol. Abstracts 19, 2189, Abs. No. 19,961 (1945).

"The tung tree, Aleurites fordii, native to China is the most important source of tung oil. Over 12 million of these trees are planted in southern U. S. A. Oiticica oil, similar to tung, comes from Licania, a native of Brazil. Other drying oils come from Lonchocarpus roseus of Mexico and Central America. Rapeseed oil for lubrication comes from Brassica napus of Argontina. Castor oil, for which there is no substitute hydraulic fluid, comes from Ricinus communis of which 10,000 additional acres are being planted in the U.S.A. A faster drying oil than tung comes from Garcia nutans which grows wild from Mexico to Venezuela." From Biol. Abstracts (abridged).

Neidig, C. P., and Burrell, Harry

THE PAINT, VARNISH, AND LACQUER INDUSTRY.

Chem. Eng. News 26, 25-7 (1948); C. A. 42, 1433 (1949). "A review of 1947." From C. A.

The anomalous situation in which tung oil is the cheapest drying oil has resulted in the return of many prowar formulations. The recently announced tung-soy copolymers are expected to find increased markets in 1948 -- "other raw materials and processing equipment are discussed."

Pepperburg, R. L.

THE SOUTH'S NEW LIQUID GOLD.

Am. Forests 45, 7-9 (1939); C. A. 33, 7600 (1939).

"A survey of the tung forests and the manufacture of tung oil in the U. S." From C. A.

Fickett, C. F.

TUNG-OIL CONSERVATION

Official Digest Federation Paint & Varnish Production Clubs No. 189, 354-66 (1939)*; C. A. 34, 2619 (1940).

"A discussion of possible methods of conserving tung oil by substitution of other oils such as oiticica or Cicoil, dehydrated castor oil and perilla. Some formulations are given to indicate the use of these oils to overcome deficiencies in viscosity, drying and water and chem. resistance due to omission of tung oil from formulations." From C. A.

Rasser, E. O.
WOOD OIL (TUNG OIL, CHINESE WOOD OIL, ETC.).
Kunststoffe 15, 111-2 (1925); C. A. 20, 299 (1926).
"Brief discussion of wood oil and its substitutes." From C. A.
Reizenstein, L. J.
OILS IN THIS WARRING WORLD.
Official Digest Federation Faint & Varnish Froduction Clubs, No.
(1900 (1941)) Brit. Chem. Abetreate 1041 P TT 101
nethous are outlined of reducing consumption of Originated in t
VIE VORSI ULLY DV USING treated drying oils of the sector
type, special resin combinations, etc." From Brit. Chem. Abstracts.
Rocca, B. T., Jr.
TUNG OIL AND FISH OIL.
Am. Paint J. 31, (8) 37-8*; C. A. 41, 604 (1947).
"The supply of tung oil will be better, while that of fish oil,
particularly sarding oil, will be very short. Perilla oil may be available in limited quantities in 1947." From C. A.
From C. A.
Scheiber, J.
THE USE OF FATS IN PAINTS AND SUBSTITUTES.
Farba u. Lack 1937.137-8*. C. A. 31.1111 (1077)
The possibilities of limiting the German consumption of
oil and linseed oil to a min. are reviewed." From C. A.
Scofield, F.
TUNG OIL ONLY "SUBSTITUTE" FOR TUNG.
Tung World 2 (1), 11, 16-7 (May, 1947).
No one has yet made a synthetic tung oil.
Shu, C. F.
TUNG-OIL FRODUCTION IN CHEKIANG.
Science (China) 16, 1158-63 (1932) (in Chinese).
Smith, W. G.
DRYING OILS.
Im. Paint J. 26, 60-3 (1941)*; C. A. 36, 919 (1942).
"The relationship of the oils used by the protective coating industries with so-celled non drains sile i
industries with so-called non-drying oils is pointed out. The use of tung oil and perilla oil is being reduced and the use of
oiticica and dehydrated castor oil is being increased. Linseed
oil has shown a very rapid increase in use." From C. A.
Smith, W. M., Jr.
AMERICAN TUNG OIL.
Chem. & Met. Eng. 49, 212-3 (1942)*; Bibliog. of Agr. 1, E, 62 (1942).
- WHE OII INCUSTIV IN AMERICA and the increasing the
of the tung tree products for their medicinal and chemical properties." From Bibliog. of Agr.
and arounds, or usi

Sorenson, S. O. DRYING OILS Paint Varnish Production Mgr. 13, 22, 24 (July, 1935)*; C. A. 29, 5679 (1935). "A discussion of the changes in the production of drying oils and some of tho problems in the development of new products from the material now available. Processing of tung oil produces an oil with excellent drying properties. Perilla, soybean and fish oils are receiving much attention as drying oils." Sun, F. C. TUNG OIL FRODUCTION IN CHEKIANG PROVINCE. Agr. Assoc. of China J. 1934 (120), 56-66 (in Chinese). Trigg, Ernest T. SUMMARY OF THE DRYING OIL SITUATION. Paint, Oil Chem. Rev. 103 (8), 18, 20, 22, 24, 26; (11), 7-10, 29-31 (1941); C. A. 35, 4228, 8323 (1941). "Statistics on the production and consumption for the last ton years of fish (except cod and cod-liver oils), linseed, tung, castor, soybean and perilla oils are given. Increased production of flax and soybeans is indicated, as well as exptl. plantings of castor beans." From C. A. Tung Growers Council of America TEXT OF TGCA BRIEF FOR TUNG TARIFF. Tung World 5 (1), 6-9 (May 1950). U. S. Bureau of the Census. ANIMAL AND VEGETABLE FATS AND OILS. 1927-U. S. Govt. Print. Off., Washington, D. C., 1932-Fublished annually; each issue compares data of four preceding years with current year. 1927/31-1940/44 have subtitle "Production, Consumption, Imports, Exports, and Stocks;" 19/11/45 to date are in Facts for Industry, Series, M17. Statistics relating to tung and other oils. Watts, E. B. WILL HISTORY REPEAT ITSELF WITH CCC. Tung World 5 (6), 6-7, 14-5 (Oct. 1950). Sales of tung oil by the Commodity Credit Corporation in 1948 are analysed and tabulated. Westgate, M. W. LATEST DEVELOFMENTS IN TUNG OIL SUBSTITUTES. Proc. Am. Tung Oil Assoc. 1944, 102 (abstract). Efforts are being made to offset the wartime lack of tung oil by (1) use of pehnolic and alkyd resins with softer drying oils, (2) increasing the unsaturation of castor and other oils, (3) segregation of the most highly unsaturated constituents of soft drying oils, (4) esterification of drying oil acids with pentaerythritol, etc. and (5) investigation of oil-bearing trees, among which Garcia nutans is the most promising as a source of excellent drying oil.

- 397 -

Williams, T. R. WHAT WILL RUSSIA DO WITH CHINA'S TUNG OIL. Tung World 4 (1), 8-9 (1949). If the Communists take over southern China they are expected to dump large quantities of tung oil on the world market for the purpose of damaging the American tung industry. Williamson, B. F.

TUNG-OIL YIELDS.

Mfrs. Record 101, (17), 24 (1932); C. A. 27, 1771 (1933). "A brief analysis is made of results in expt. stations. A yield of 675 lb. of oil per acre is estd. for a grove at Gainesville, Fla." From C. A.

Wong, L. S.

OUTLOOK OF CHINA'S TUNG OIL TRADE IN 1948. China Trade Monthly 2, 67-70, 128-30 (Jan., 1948)*

Woods, S. C.

ADDRESS

Proc. Am. Tung Oil Assoc. 1946, 13-7.

The exportation of Chinese wood oil from China is expected to be below normal for a few years because of several conditions resulting from the war, namely, a lack of river boats, inflated costs of production and handling of the oil in China and the migration inland during the war of personnel trained to handle wood oil.

PATENT LITERATURE

VIII. HEAT BODYING OF TUNG OIL FOR COATINGS

Arsem, W. C. (to General Electric Co.)

PROCESS OF TREATING OILS AND OTHER CLYCERIDES.

U. S. 1,760,535 (May 27, 1930); C. A. 24, 3661 (1930). "A glyceride of an unsatd. fatty acid such as linsced, China wood, perilla or soy-bean oil is heated in the presence of a substance contg. an amine radical, such as 1% of benzidine, in order to accelerate polymerization." From C. A.

Auer, L.

A PROCESS FOR THE MODIFICATION OF THE FHYSICAL PROPERTIES OF FATTY OILS CONSISTING OF OR CONTAINING UNSATURATED HIGH MOLECULAR ACIDS.

Brit. 321,689 (Nov. 4, 1929); C. A. 24, 2910 (1930).

"In modifying the physical properties of org. unsatd. compds. described in Brit. 287,943 (C. A. 23, 490), fatty oils such as tung, linseed, castor, fish, sunflower, rapesced, pine, corn and olive oils are heated under reduced or atm. pressure with modifying agents such as NaHCO₃ to form a hardened product. The effect is increased by the addn. also of BaO₂. A resin such as colophony may be added to prevent frothing, and various specified, modifying, plasticizing and coloring substances also may be added. Products obtained may be vulcanized with S or S chloride, and are suitable for use in varnishes and lacquers." From C. A.

Auer, L.

IMPROVEMENTS IN AND RELATING TO THE MODIFICATION OF ISOCOLLOIDS CONSISTING OF OR CONTAINING HIGH MOLECULAR UNSATURATED ORGANIC ACIDS.

Brit. 337,732 (Oct. 24, 1930); C. A. <u>25</u>, 2312 (1931).

"Materials such as linseed or China wood oil or their fatty acids are heated to above 250° (or thickened oils or tung oil to above 200°) with 2-10% of a primary aromatic diamine or a monoamine of high mol. wt. or both, such as m-phenylenediamine, p-tolyenediamine, β -naphthalyamine or p,p'-diamines such as p-p'-diaminodiphenylamine or p,p'-diaminodiphenylurea. Various other substances may be added and the products may be vulcanized with or without use of an accelerator or activator." From C.A.

Badenol, G. m. b. H.

PROCESS FOR THE PREPARATION OF WOOD-OIL STANDOIL. Ger. 622,369 (May 24, 1934); C. A. 30, 1556 (1936). "Wood oil is treated with O₃ and then heated to about 150°." From C. A.

Badger, W. L.

POLYMERIZATION OF DRYING OILS.

U. S. 1,811,290 (June 23, 1931); C. A. <u>25</u>, 5048 (1931). "Oil such as linseed or China wood oil is circulated at a rapid rate from a vessel under reduced pressure through a heater and back to the vessel, and is rapidly heated as it passes through the heater. App. is described." From C. A. Backeland, L. H. (to General Bakelite Co.)

TREATING TUNG OIL AND COATING OR IMPREGNATING OBJECTS THEREWITH. U. S. 1,312,093 (Aug. 5, 1919); C. A. 13, 2579 (1919).

"Articles such as paper or elec. coils are coated with tung oil which has been preliminarily heated to about 200° and then (after application to the article to be coated) solidified by heating to a lower temp., e.g., a temp. of about 150-160°. The articles may be given an exterior coating of a phenolic condensation product rendered insol. and infusible." From C.A.

Berger, H. G., Crandall, G. S., and Socolofsky, J. F. (to Socony-Vacuum Oil Co.) PROCESS OF DISPERSING OIL GELS.

U. S. 2,418,920 (Apr. 15, 1947); C. A. <u>41</u>, 4657 (1947). This patent covers the use in varnishes of the gelled oils prepared as described in U. S. 2,419,921.

Berger, H. G., Crandall, G. S., and Socolofsky, J. F. (to Socony-Vacuum Cil Co.) FROCESS OF BODYING DRYING OILS AND THE FRODUCT RESULTING THEREFROM. U. S. 2,418,921 (Apr. 15, 1947); C. A. <u>41</u>, 4657 (1947).

> "Certain drying oils are polymerized or gelled and then dispersed in an unbodied oil for use in making varnishes, undercoaters, and enamels. * * * Preferred cils for gelling are oiticia, perilla, and dehydrated castor oil. They are gelled by heating to 500° F. with a catalyst such as BF2 or HF. Metallic catalysts should not be used because they adversely affect film properties. Preferred catalyst concns. are 0.1 to 1.0%. Gels formed from China wood oil by using a catalyst could not be dispersed in unbodied oils, whereas gels of China wood oil prepd. by heating alone could be dispersed but yielded inferior products. The slower drying oils, such as linseed, soybean, or fish oils, gelled catalytically but yielded inferior products. However, when the gels from the preferred oils were combined with any of the slower-drying oils in quantities 50% or greater superior varnish bases were formed. The gels resembled art gum and, when milled into small particles, the "crumbs" of art gum. In the process of dispersing the gelled oils in an unbodied oil dispersing agents, such as quinoline, or pyridine, may be used but are not absolutely necessary. An example of the process is: oiticia oil is gelled by the addn. of 0.1% BF2 and heating for 5 to 10 min. to obtain a product resembling aft gum; 50 pts. of this gel and 150 pts. of linseed cil are mixed in a Waring blendor; to this gel-oil are added 100 pts. of ester gum and 0.4 pts. isoquinoline (as dispersing agent); the entire mixt. is heated with stirring for 95 min. at 560° F. after cooling to 400° F. 450 pts. of petroleum thinner and driers are added. The resulting varnish was found to have good phys. and drying properties. Particular application of this process was found in using the slower drying and semidrying oils, such as soybean and linseed oils. In this way replacement of scarce tung oil with more plentiful oils was made possible without sacrificing any of the favorable properties of tung-oil varnishes." From C. A.

Beringer, A. (Firm)

PROCESS OF PREVENTING THE GELATINIZATION OF WOOD OIL ON HEATING.

Gur. 261,403 (Sept. 27, 1912)*; C. A. 7, 3244 (1913).

"For the purpose of preventing coagulation of wood oil upon heating, S, sulfides, Se or schinides, are added to the wood oil, alone or in admixt., operating at a low temp. or at temps. above 300°. The application of the wood oil in the varnish and linoleum industries is thereby extended. The varnishes prepared with such wood oil are water-resistant and do not form skins. Details of prep. are specified." From C. A.

Boringer, A. (Firm)

A PROCESS OF PREVENTING WOOD OIL FROM COAGULATING UNDER THE INFLUENCE OF HEAT.

Brit. 21,725 (June 4, 1914); C. A. 9, 972 (1915).

"Treating wood oil to render it incapable of coagulating when heated, and suitable for the prep. of varnishes, by the addition of small quantities of Se, S, a selinide, or a sulfide, or any mixt. of these substances. When boiled, wood oil so treated yields a product of honey-like consistency, from which the free fatty acids, apparently polymerization products, may be isolated. The oil may be directly converted into lacquers by the addition of resins." From C. A.

Boringer, E., and Zimmer, W. (to Reichhold, Flugger & Boeking) PROCESS OF PRESERVING WOOD OIL FROM CONGEALING ON BEING SUBJECTED TO HEAT.

> U. S. 1,103,473 (July 14, 1914); C. A. 8, 3127 (1914). "The process consists of adding about 1% of S or 0.5% of Se to the wood oil." From C. A.

Bonny, R. D., and Egge, W. S. (to Congoleum-Nairn, Inc.) METHOD OF TREATING CHINA-WOOD OIL AND PRODUCT THEREOF.

U. S. 2,133,889 (Oct. 18, 1938); C. A. 33, 886 (1939).

"An uncoagulated oxidized product suitable for use in coating compns., etc., is obtained by a process which involves admixing the China-wood oil with castor oil, subjecting the mixt. at an elevated temp. but below 120° to an oxidizing treatment limited substantially to the formation of uncoagulated products of oxidation, and extg. with alc. the mixt. of fluid oxidized China-wood oil and castor oil to sep. the castor oil therefrom, the castor oil being present during the oxidation step in an amt. that is effective substantially to retard the coagulation of the China-wood oil, a sufficient amt. of the alc. remaining occluded by the oxidized China-wood oil to maintain the oxidized China-wood oil in fluid condition during and at the conclusion of the extn. operation." From C. A.

British-Thomson-Houston Co. (Scheiber, W. J.)

IMPROVEMENTS IN AND RELATING TO PROCESSES OF TREATING DEVING OILS. Brit. 319,218 (Jan. 19, 1931); C. A. 24, 2623 (1930).

"About 1% of benzidine, diphenylamine, m- or p-phenylenediamine, diisopropylamine or other suitable amine is added to facilitate formation by heating of a "boiled," "gelled," or "degelled" product from oils such as linseed, China-wood, perilla, soy-bean or cottonseed oil, or to facilitate condensations such as those involving phthalic acid and acids derived from drying oils, etc." From C. A. Buckmaster, B. S. (to Donolac Corp.)

METHOD OF CONVERTING DRYING OILS TO NONDRYING OILS.

U. S. 2,061,829 (Nov. 24, 1936); C. A. <u>31</u>, 893 (1937). "A drying oil of the vegetable or animal oil group, such as tung oil, is heated from an external source with about 0.125-0.5% of elemental S or a S compd. such as S₂Cl₂ to a temp. of about 260-400° and a nonoxidizing gas such as CO₂ is then passed through the oil to reduce the S content until the product is compatible with lacquer-type resins and nitrocellulose." From C. A.

Cabot, S.

IMPROVEMENTS IN OR RELATING TO THE FOLYMERISATION OF OILS. Brit. 250,538 (Feb. 10, 1926); C. A. 21, 1194 (1927). "Tung oil and similar oils are polymerized without gelatinization by heating while dispersed in a non-volatile solvent, e.g., linseed oil, which polymerizes at a slower rate if at all. A temp. of 300° may be used and the product may be employed in making paints, stains, varnishes, or enamels." From C. A.

Canadian Industries, Ltd. (Booge, J. E.)

DRYING-OIL COMPOSITION.

Can. 305,163 (Oct. 28, 1930); C. A. 25, 834 (1931). "To make a permanent mixt. of nitrocellulose and a drying oil (linseed, China wood or perilla) the hot oil is blown with air, which results in a drop in the I no. of the oil, accompanied by an increase in the viscosity that renders the oil completely miscible with pyroxylin jelly, and then the blown oil is mixed with nitrocellulose. This compn. is used in the manuf. of artificial leather, films, etc." From C. A.

Ceplan, Solomon (to Harvel Research Corp.)

FOLYMERIZATION OF DRYING OIL.

U. S. 2,176,058 (Oct. 17, 1949); C. A. <u>34</u>, 1202 (1940).

"Diethyl sulfate (suitably in a proportion of about 5-10%) is dissolved in China wood oil then heated to about 105° to effect desired polymorization, as for use in varnishes, molded products, etc. (the diethyl sulfate serving to promote polymerization)." From C. A.

Chemischtechnisches Laboratorium Meffert

PROCESS FOR THE CONVERSION OF WOOD OIL INTO A SMOOTH, V/RNISH-LIKE AND HARD DRYING PRODUCT.

Ger. 211.,405 (Sept. 8, 1908); C. L. 3, 2633 (1909).

"Transforming wood-oil into a varnish-like, smooth hard drying product, by heating it for a short time above the polymerization temp., taking care to stir the mass constantly." From C. A.

Cowan, G. H.

I FROVEMENTS IN AND RELATING TO COLTING COMPOSITIONS AND METHODS OF PREPARING THE SAME.

Brit. 477,904 (Jan. 10, 1938); C. A. 32, 4808 (1938).
 "These comprise a nonferrous metal powder, e.g., of Cu, Al,
 Zn, or Pb, in a liquid vehicle comprising China wood oil to which

has been added while hot an acetate, preferably (AcO)₂Co. The acetate treatment prevents jelling of the oil. The compn. may contain Pb oxide to prevent electrolysis, a resin, e.g., PhOHCH₂O or other phenolic resin, kauri gum, or esterol. It may contain a drier, e.g., Mn linoleate and other compds. of Mn, Co, and Pb. Other ingredients specified are boiled linseed oil, xylene, dipentene, turpentine, C₆H₆, benzine, ZnO, Fe oxide, Cr oxide, HgO, ZnCrO₁ and silex." From C. A.

Dent, H. M. (to General Plastics, Inc.)

DRYING-OIL COMPOSITICN.

U. S. 2,064,786 (Dec. 15, 1936); C. A. <u>31</u>, 893 (1937).

"A drying oil such as China wood oil is heated to about 230-290° with p-dihydroxydiphenyl ethane or the like, etc., until a homogeneous liquid product is obtained which does not sep. on cooling: The resulting product may be used as a baking varnish." From C. A.

Depew, H. A.

METHOD OF MODIFYING ORGANIC CHEMICAL MATERIALS.

U. S. 2,280,802 (Apr. 28, 1949); C. A. 36, 5662 (1942).

"Materials to be polymerized are dispersed as a spray in a carrying gas and are polymerized while surrounded by a carrying gas so that the product does not come into contact with the walls of the reaction chamber." From C. A.

Donovan, L. A., and Daniels, E. A.

METHOD OF TREATING CHINA WOOD OIL.

U. S. 2,094,590 (Oct. 5, 1937); C. A. <u>31</u>, 8964 (1937).

"About 0.1-0.2% of S is added to China wood oil to prevent jellification of the oil by subsequent treatment, and the oil is then heated in the presence of the S to at least 250° for a sufficient time (which may be about 15 min.) to render the oil nondrying, and air is then passed through the oil to render it compatible with the usual ingredient of nitrocellulose lacquer." From C.A.

Du Pont de Nemours, E. I., & Co.

IMPROVEMENT IN THE PREPARATION OF BETA-ELEOSTEARIN AND OF COATING COMPOSITIONS CONTAINING THE SAME.

Brit. 312,052 (July 15, 1930); C. A. 24, 980 (1930).

" β -eleostearin, obtained as an insol. solid by the action of light or of chem. agents such as an I soln. on china wood oil, is rendered sol. in solvents such as gaseline or naphtha by heating it to about 260°. The solns. may be used as varnishes with or without addn. of various other varnish ingredients. Several examples are given." From C. A.

In C. a. the name of the inventor is given as C. G. Gauerke although his name does not appear in the final patent.

Ellis, C. (to Ellis-Foster Co.)

ALTERED TUNG OIL AND PROCESS OF MAKING SAME.

U. S. 2,101,791 (Dec. 7, 1937); C. A. 32, 1124 (1938).

"By heating tung oil to about 100-150° with an admixt. of about 5-15% of orcinol, phloroglucinol, resorcinol, pyrocatechol, or hydroquinone in the presence of an acid condensing agent such as oxalic acid, a compn. is obtained which is thicker than the original raw oil and is miscible with glyceride oils and when dissolved in a solvent to which driers are added dries in thin films to a frost-free surface. Numerous examples are given." From C. A.

Gauerke, C. G. (to Du Pont de Nemours, E. I., & Co.) COATING COMPOSITION CONTAINING BETA-ELEOSTEARIN. U. S. 1,898,088 (Feb. 21, 1933); C. A. <u>27</u>, 2830 (1933). "Heat-treated β-eleostearin which is sol. in high-boiling gasoline is used in compns. with synthetic resins, drying oils, gasolines, etc., to form quick-drying coatings." From C. A.

Goiger, T. H., and Burgess, L. M. (to Tung Oil Products, Inc.) BODIED TUNG OIL AND PROCESS OF MAKING THE SAME. U. S. 2,084,137 (June 15, 1937); C. A. <u>31</u>, 5605 (1937). "Tung oil is heated together with an inert removable diluent, such as high-flash coal-tar naphtha, to a temp. above 260° (suitably to about 310°) to effect an appreciable thickening of the oil, and the diluent is then removed from the oil." From C. A.

Grucnwald, L. A., and Reider, M. J. (to Gruenwald, L. A.) DEODORIZATION AND REFINING OF TUNG OIL.

U. S. 2,276,233 (March 10, 1942); C. A. <u>36</u>, 4726 (1942). "Various operative details are given which may involve heating the oil first with a small quantity of an aq. soln. of a Na sulfite dispersed throughout the oil and then with a small quantity of an aq. soln. of Pb acetate (suitably with heating to 110° followed by diln. with heavy naphtha and filtration with the use of a vacuum and infusorial earth)." From C. A.

Gustav Ruth Akt .- Ges., and Asser, E.

PROCESS FOR THE TREATMENT OF DRYING OILS.

Fr. 694,074 (Sept. 9, 1930); C. h. 25, 2011 (1931).

"Useful products are obtained by heating drying oils, particularly linseed oil or a mixt. of linseed oil and china wood oil, to about 270-280° until polymerization commences. Air is then bubbled through and the heating continued to 310° or more. Cellulose esters or ethers may be added." From C. A.

Hall, Gustav

PRODUCTION OF A NON-GELLING WOOD OIL PRODUCT.

Ger. 434,202 (Sept. 24, 1926)*; Chem. Zentr. 1926, II, 2951. Wood oil is prepared for use in varnish by heating it at a temperature below 200° until gelation occurs, then heating it at 250-300° until it becomes liquid again.

Haller, Wilhelm

PROCESS FOR THE WORKING UP OF GELATINIZED WOOD OIL. Ger. 114,400 (June 30, 1899).

Chinese wood oil possesses the property of gelatinizing on prolonged heating above 200° C. to a rubber-like solid, insoluble

in common solvents and, hence, useless for the preparation of varnishes. This patent describes a method of dissolving this gel by melting it at above 300° with poppyseed oil or nut oil to yield a product, soluble in turpentine, benzene, acetone, amyl acetate, etc., and miscible with oil varnishes, pyroxylin solutions and drying oils.

Haller, Wilhelm

PROCESS FOR THE PRODUCTION OF SOLIDIFIED WOOD OIL (ALEURITIS OIL). Austria 1394 (Fob. 15, 1900).

Tung oil is gelled by heating at 200° in a solvent.

Haller, Wilhelm

PROCESS FOR THE ARTIFICIAL AGING OF LINSEED OIL.

Ger. 601,353 (Feb. 10, 1933); C. A. 29, 948 (1935).

"Crude fresh linseed oil is heated, e.g., to 80-120° for 1-1.5 hrs., with up to about 20% of a polymerized oil, e.g., stand oil or polymerized wood oil, soybean oil, or castor oil. The sepn. of mucilaginous impurities when the oil is boiled to form stand oil or varnish is thus avoided." From C. A.

Harper, Walter J. (to Glidden Co.)

TREATMENT OF TUNG OIL.

U. S. 2,152,642 (Apr. 4, 1939); C. A. <u>33</u>, 5209 (1939).

For the obtainment of a smooth, glossy rapid-drying oil, tung oil is heat-treated in the presence of S, Se or a sulfide or selenide, which retards the heat gellation and drying of the oil (suitable at a temp. at about 300° for 15 min.) and the oil is then treated with a solvent such as AmOH and EtOH which is miscible with the oil when hot but not when cold and which serves on its sepn. to remove the previously used treating chemical.

Harvey, M. T. (to Harvel Corp.)

COMPOSITION OF MATTER AND METHODS AND STEPS OF MAKING AND USING THE SAME.

U. S. 1,838,076 (Dec. 22, 1931); C. A. 26, 1459 (1932) (No abstract) The making of varnishes from China wood oil and cashew nut shell liquid are described. In the presence of the latter China wood oil can be bodied at 600° with little danger of gelation. China wood oil which has gelled due to excessive cooking can be readily dispersed by warming it with an equal amount of the cashew nut shell liquid. In one example, cashew nut shell liquid (20), China wood oil (40) and linseed oil (4), are cooked at 500-600° F. to give a product which, with or without driers or rosin, will dry to a hard, flexible surface useful for varnishes or insulation.

Hills, L. H. (to Vellumoid Co.)

SATURATED FIBROUS MATERIAL AND SATURANT AND METHOD OF MAKING THE SAME.

U. S. 2,172,974 (Sept. 12, 1939); C. A. <u>34</u>, 556 (1940).

"Tung oil is heated to about 280° and then, before gelation occurs, cooled rapidly to below 175° in the absence of resin." From C. A. IMPROVEMENTS IN IMPREGNATED FIBROUS MATERIAL AND IMPREGNATING COMPOSITION AND METHOD OF MAKING THE SAME.

Brit. 522,892 (July 1, 1949); C. A. <u>35</u>, 6111 (1941).

"Tung oil bodied without the use of resins, in amt. by wt. at least twice the amt. of chlorinated rubber (Tornesit) and a mutual solvent, such as toluene, is used as an impregnating compn. for paper. The material is dried below 160° to remove the solvent and set the gel to a non-tacky condition. The tung oil is bodied at 540° F. and before gelation occurs the oil is cooled rapidly to below 350° F. An antioxidant (about 2% of the amt. of the oil) is preferably added." From C. A.

Imperial Chemical Industries, Ltd. (Morgan, H. H., and Drummond, A. A.) IMPROVEMENTS IN AND RELATING TO THE TREATMENT OF TUNG OIL / ND MIXTURES CONT INING THE S. ME.

Brit. 329,685 (May 19, 1930); C. A. <u>24</u>, 6040 (1930).

"Raw tung oil (which may be mixed if desired with linseed or perilla oil or a natural or synthetic resin) is heated to 150° or higher for several hrs. in the presence of an org. solvent of non-film-forming character such as cyclohexanol, benzyl alc., tetrahydronaphthalene or kerosene, and a small quantity of a dehydrating chloride such as ZnCl₂ or of KHSO₄ is added. The product dries with a smooth, clear, glossy surface. Examples of the treatment with details are given." From C. A.

Kass, P., and Nichols, J. (to Interchemical Corp.)

DRYING OILS.

U. S. 2,497,904 (Feb. 21, 1950); J. Am. Oil Chemists' Soc. -27, 152 (1950).

"The drying properties of mixtures of tung oil with other drying oils are improved by refluxing the mixture with acetic anhydride at 160-180° and removing the anhydride." From J. Am. Oil Chemists' Soc.

Knoche, L.

IMPROVEMENTS IN THE MANUFACTURE OF AN OIL AND OF A VARNISH PREPARED THEREFROM.

Brit. 24,224 (Feb. 29, 1896); J. Soc. Chem. Ind. 15, 284 (1896). "200 lb. of oil pressed from the berries of a tree called "Abura Giri" or "Japanese wood oil," are boiled until a temperature of 205° C. is reached, and maintained at this temperature for three hours tor ender the oil of greater density. It is then cooled down to 180° C., and 70 lb. of naphtha or turpentine are thoroughly mixed with the oil to cause it to flow freely. Linseed oil may also be mixed with the raw oil and treated in the same manner. The oil compound produced is said to be superior and more durable than either linseed or cotton seed oils. A mixture of equal parts of this oil compound and ordinary Varnish is said to produce a new varnish, which is superior in finish and brilliancy." From J. Soc. Chem. Ind. Kronstein, Abraham

M/NUF/CTURE OF V/RNISHES AND PRODUCTS RESEMBLING BALSAMS. Brit. 17,378 (1900) (Sopt. 28, 1901); J. Soc. Chem. Ind. 20, 1123 (1901).

"The process claimed, consists of heating a fatty oil or other unsaturated organic compound to a temperature short of decomposition, with the exclusion of oxygon or any oxidizing agent, so that polymerized substances of high molecular weight are produced. The process may be applied to the manufacture of varnishes from drying oils, fish oils, rapeseed oil, castor oil, etc. Of other unsaturated organic compounds suitable for the purpose, the following are among those chiefly employed: Allyl cinnamate, styracin, allyl- and diallyl malonates, or "allyl salts of substituted malonic acid, of indene, and of substances of the type of eugenol, safrol, iso-eugenol, and styrol and its substitution products."

An admixture of 50 percent of Japanese wood oil with oils ordinarily used in the manufacture of varnishes yields a product of the consistency of "stand oil," when thus heated to a temperature below the decomposition point.

The substances formed vary with the nature of the compounds used. Thus, amber-like products are obtained from bodies of the type of allyl cinnamate, styracin, and allyl or diallyl malonate. A compound resembling glass with the properties of a resin is yielded by styrol and its derivatives, whilst esters of diallyl malonic acid produce a substance resembling natural balsam, which is soluble in the ordinary solvents. Allyl cinnamate or diallyl malonate are converted into resin-like bodies which are soluble in benzene and ethylene bromide, but insoluble in alcohol and ether.

By heating a solution of styracin in allyl cinnamate, in the absence of oxygen, a compound resembling Peru balsam is formed, whilst safrol, eugenol, iso-safrol and iso-eugenol give soluble solid substances resembling natural soft resins.

A special claim is made for the manufacture of oil of high viscosity, by heating wood oil, or mixtures containing more than 50 per cent of that oil, with other oils, or unsaturated organic compounds, in the absence of air, to about 200° C. until solidification occurs, and then raising the temperature to 300° C. until the mass liquefies, forming an oil which only becomes hard when exposed to the air." From J. Soc. Chem. Ind.

Kronstein, Abraham

IMPROVEMENTS IN OXIDIZING CHINESE WOOD OIL AND MIXTURES THEREOF. Brit. 1386 (1901) (Mar. 23, 1901); J. Soc. Chem. Ind. 20, 485 (1901).

"The object of this patent is to provent the coagulation which occurs on treating this oil with oxidizing agents. The oil is mixed with a resin', drying oil, or solvent in certain specified proportions, and the mixture heated with an oxidizing agent. Or the wood oil or mixture may be solidified by heating it with another oil, or a resin or solvent, and the solid product further mixed with a resin, drying oil, or solvent, and oxidized." From J. Soc. Chem. Ind. Kronstein, Abraham

IMPROVED PROCESS FOR THICKENING CHINESE WOOD OIL AND MANUFAC-TURING SUBSTITUTES FOR HARD RESINS THEREFROM. Brit. 1387 (1901) (Jan. 16, 1902); J. Soc. Chem. Ind. 21, 264 (1902).

"If wood-oil be heated, preferably with exclusion of air, for a certain time to a temperature of about 200° or 250° C. with a certain proportion of some resin such as dammar, the mixture eventually becomes viscid and solidifies even while hot; and it finally forms a material which is insoluble in ordinary resin-solvents until after it has been melted at a higher temperature (about 300° C.), resembling copal and amber in this particular, and being a perfect substitute for them. If, however, a proportion of the resin larger than is required to induce solidification at 200° C. be added to the wood-oil, or if the heat be too low or not sufficiently prolonged, the mixture remains liquid and does not solidify till it is cold, when it is still soluble in turpentine, benzene, and oil of camphor, and is distinguished by a high degree of elasticity. Thus the solidified products may be employed in the manufacture of varnishes in place of the usual expensive hard resins; while the non-solidified products can be used to prepare commoner varnishes and japans, or in the manufacture of linoleum. The proportion of resin needed to determine insolubility varies according to the nature of the resin adopted, being about 50 per cent. in the case of dammar, Venice turpentine, amber, gutta-percha, and asphaltum; 70 per cent. in the case of copal; and only 30 per cent. in that of colophony. For certain purposes, mixtures of resins, or of resins and linseed or other drying oils, may be added to the wood oil. Presence of air during the process causes oxidation and decomposition, and renders the finished material dark in colour. Brit. Pat. 17,378, 1900, is referred to (this Journal, 1901, 1123)." From J. Soc. Chem. Ind.

Kronstein, Abraham

IMPROVED PROCESS FOR THICKENING CHINESE WOOD OIL AND MANUFAC-TURING SUBSTITUTES FOR HARD RESINS THEREFROM. Brit. 1387 (1901) (Jan. 16, 1902).

"The herein described process for thickening wood oil and making therefrom bodies of very high consistence and soluble only when remelted by dissolving resins or mixtures thereof in wood oil, and heating the solutions thus obtained to 200° to 250° C. preferably with exclusion of air." Claim No. 1 of patent.

Kronstein, Abraham

PROCESS FOR TREATING WOOD OIL WITH OXIDIZING AGENTS.

U. S. 833,063 (Oct. 9, 1906); C. A. 1, 370 (1907).

A process is described which claims to prevent the coagulation of tung oil which normally occurs when tung oil is combined with oxidizing oxygen-yielding driers. Coagulation may be avoided by mixing the tung oil with varnish-forming materials, such as drying oils and resins, using sufficiently low proportions of tung oil that gelatinization does not occur on quick heating to 270-280° C. An oxidizing agent which may be any oil-soluble oxygen carrier, is added to the hot mixture. Before coagulation occurs the oil is cooled, quenched with solvent, and refluxed for some time. A second process cells for heating compositions high in tung oil with driers until coagulation occurs. The gelled mass is then dissolved by heating it with drying oils other than tung oil until liquefaction takes place.

Kronstein, Abraham

MANUF CTURE OF V RNISHES, BALSAMS, AND RESINS. U. S. 843,401 (Feb. 5, 1907).

This process for the production of solid resins and balsams consists of heating unsaturated organic compounds below their decomposition temperature and in the absence of oxidizing agents. Oils which may be used include allyl cinnamate, monoand diallyl malonate, eugenol, safrol, heavy camphor oil, styracin, Chinose wood oil, linseed oil, camelina oil, rape oil, cotton oil, maize oil, etc. Of the natural oils, only wood oil yields hard, solid products. The latter retains some elasticity even on prolonged heating.

Lystnd, Birger

BOILED WOOD OIL.

Norw. 57,364 (Dec. 21, 1936)*; C. A. <u>31</u>, 2842 (1937). "The oil is heated in a container resting on a heating element and provided with a hinge, whereby the heated oil, after it has attained the desired viscosity, is poured from the vessel into one or more containers wherein it is quickly cooled or mixed with cold oil or other varnish ingredients." From C. A.

McKinney, R. S., Rose, W. G., and Freeman, A. F. (to United States of America) TREATED TUNG OIL.

U. S. 2,277,342 (March 24, 1942); C. A. <u>36</u>, 5039 (1942). "A clear oil is prepd. by subjecting a "petr. ether" solventextd. tung oil to a temp. of at least 200° for about 30 min." From C. A.

Mayer, F.

PROCESS FOR THE THICKENING OF WOOD OIL AND RELATED OILS. Swiss 62,355 (Feb. 18, 1913); C. A. <u>8</u>, 2270 (1914). "In a process of thickening wood oil and related oils, the material, with exclusion of air, is heated quickly above its coagulation temp. to temps. up to 300°." From C. A.

Novak, Izador J. (to Raybestos-Manhattan, Inc.)

VARNUSH OIL.

U. S. 2,318,009 (May 4, 1943); C. A. <u>37</u>, 6146 (1943).

"A process is employed for producing a relatively pale, amber colored, heat embodied, air-blown varnish oil, of high waterproofness, tough film formation, and good adherability to metals ("an oil of the China wood oil type") which involves subjecting a drying oil of the nonconjugated type, such as linseed oil or soybean oil, to filtration through absorptive earth, prior to or without appreciable chem. treatment, to reduce its ash content to about 0.01-0.001%, thereafter subjecting it to controlled low-temp. air blowing to form an oil of conjugated system fluid at 25°, and heating the conjugated oil at about 500-600° F. to form a varnish oil of desired finished viscosity." From C. A. Olwerke Noury, and Van der Lande, G. M. B. H.

PROCESS FOR THE PRODUCTION OF THICKENED DRYING OIL.

Ger. 606,869 (Nov. 13, 1929); C. A. 29, 3863 (1935)

"Drying oils are thickened by heating to 200-320° with finely divided Pt, Pd, Ni, or Co. The heating may take place in the presence of inert gases, at normal or raised pressures, or in vacuo. In examples, linseed or wood oils are heated with a Ni catalyst, (HCOO)₃Ni or Pt-asbestos. The viscous products are used in the lacquer industry." From C. A.

Phillips, J. W.

COLLOIDAL SUSPENSION OF POLYMERS AND PROCESS OF MAKING THE SAME. U. S. 1,395,242 (Oct. 25, 1921)*; C. A. 16, 651 (1922).

"Tung oil dissolved in a solvent such as turpentine is heated to 100° with a small addition of Fb resinate; the materials are filtered and then treated with a current of air at room temp. for 8-20 hrs. to effect polymerization and obtain a material adapted for waterproofing textile or other fabrics. A small amt. of rosin glycerol esters may be added before the polymerization to a t as a stabilizer and preventive of coagulation; or other stabilizers such as CS_2 , S, or S chloride may be used. The product may be forced into paper, wood, leather, canvas, or other fabrics under pressure to render them repellent to H_2O and oils; or may be applied in soln. in a volatile solvent such as gasoline, acetone, turpentine or AmOAc or mixts. of these. Mineral pigments, lakes or aniline dyes may be added to the mixts. and products of greater capacity or milkiness are obtained by polymerizing the tung oil with S or S chloride." From C. A.

Pillnay, Franz

PPOCESS FOR THE PRODUCTION OF WOOD-OIL STANDOIL. Ger. 560,702 (June 28, 1929); C. A. 27, 1217 (1933). "Thickening oil for lacquers is made by heating wood oil to 300° with AcOH and nitrosodiphenylamine in complete absence of atm. O. App. is described." From C. A.

Plank, Charles J. (to Socony-Vacuum Oil Co.)

CATALYTIC ISOMERIZATION OF UNSATURATED GLYCERIDE OILS.

U. S. 2,435,695 (Feb. 10, 1948); C. A. <u>42</u>, 2786 (1948). "To promote structural isomerization, drying and semidrying oils are heated to 450-600° F. for 1-2 hrs. with a BF₃-bodied

china-wood oil gel as catalyst." From C. A.

Plummer, H. L., and Stone, L. F. (to Du Pont de Nemours, E. I., & Co.) CURED TUNG OIL ACID.

> U. S. 2,011,908 (Aug. 20, 1935); C. A. <u>29</u>, 6780 (1935). Tung oil acids are heated to about 280-305° to obtain a product which forms non-frosting coatings.

Pratt, M. F., Apjohn, T. L., and Happel, John (to Socony-Vacuum Oil Co.) VARNISH MANUF/CTURE.

U. S. 2,283,872 (May 19, 1942); C. A. <u>36</u>, 6364 (1942). "An elec. alloy heated app. used is described, and a continuous process is employed for heat-treating film-forming material comprising quick-drying oil whereby the material possesses tendencies to get when heated in a continuous manner under bodying conditions of temp. and time and in which the material consists essentially of a film-forming drying oil or a mixt. of drying oil with a resin which involves maintaining a relatively large quantity of the material at a nongolling temp. above the max. temp. at which the untreated material will gel from heat, maintaining all portions of the large quantity of material above the max. temp. and in a wellagitated state, continuously adding a relatively small quantity of the material to be treated to the relatively large quantity in a sufficiently low ratio that the added quantity is heated above the max. temp. at which gelation occurs in less time than is required to get the material at any temp. from heat, and continuously withdrawing a relatively small quantity of heated material from the relatively large quantity in such ratio and under such conditions that heated material remains at a temp. above the max. temp. long enough to remove its tendencies to gel under bodying conditions of temp. and time but not long enough to substantially impair its quick-drving property." From C. A.

Pungs, W. (to I. G. Farbenind. A.-G.)

OXIDIZING MIXED FATS, OILS, WAXES AND RESINS.

U. S. 1,780,632 (Nov. 4, 1930); C. L. 25, 226 (1931).

"A retort is charged with inert heat-cond. material such as Raschig rings and a mixt. to be oxidized such as resin or China wood oil and lignite wax is fed into the retort to such a point below the top of the inert charge so that when the mixt. swells during the reaction it will be in contact with the inert material, and a strong current of air is passed through the mixt. at a temp. of about 160-70° to effect oxidation. App. is described." From C. A.

Reece, F. M. (to O'Brien Varnish Co.)

NON-DRYING OIL AND PRODUCT THEREOF.

U. S. 1,903,656 (April 11, 1933); C. A. <u>27</u>, 3350 (1933). "A coating compn. comprises a sol. lacquer base such as cellulose nitrate or acetate and a non-drying liquid oil product such as China wood oil which has been heated as high as 330° in the absence of gelatinization-inhibiting substances and for so short a time as to avoid gelatinization while reducing the n to a point below 1.499." From C. A.

Reece, F. M. (to O'Brien Varnish Co.)

TREATMENT OF CHINA-WOOD OIL TO PRODUCE A LIQUID UNGELLED OIL AND PRODUCT THEREOF.

U. S. 1,903,686 (April 11, 1933); C. A. 27, 3350 (1933).

"The oil is rapidly forced through a conduit of such restricted cross-sectional area as to permit a rapid input of heat and the conduit is heated to bring the oil to a temp. of at least about 330° in a period of time sufficient to secure substantial reduction of the n of the oil and so short as not to permit gell formation (suitably a period of about 15 sec. for a temp. of about 350° for a product having drying properties) and the oil is then rapidly cooled." From C. A. Reece, F. M. (to O'Brien Varnish Co.) TREATMENT OF CHINA WOOD CIL TO PRODUCE A LIQUID UNGELLED OIL AND PRODUCT THEREOF. U. S. Reissue 19,307 (Sept. 4, 1934); C. A. <u>28</u>, 6579 (1934). A reissue of original patent U. S. 1,903,686 (C. A. <u>27</u>, 3350 (1933).

Reece, F. M., and Taggert, M. F.

UNGELLED DRYING OIL PRODUCT SUITABLE FOR VARNISHES, ETC. U. S. 2,113,358 (Apr. 5, 1938); C. A. <u>32</u>, 4364 (1938).

"/ liquid ungelled product comprises a jointly heat-treated mixture of a gelling drying oil such as tung oil and at least one other drying oil such as soybean oil, the gelling oil being at least 10% and the other oil or oils being at least 10% of the mixture, the oils having been jointly rapidly heated to bring the mixt. to a temp. of at least 330° under superatm. pressure in a time sufficient to secure substantial reduction of the <u>n</u> and increase of sp. gr., acid no. and viscosity of the oils, and so short as not to permit gel formation, the period being suitably of the order of twenty-two seconds for a temp. of about 355°, and the resulting product having a substantially higher viscosity than a mixture of the same oils in the same proportion individually subjected to the same heat treatment." From C. A.

Reisert, Hans .

PROCESS FOR PREVENTING THE GELATION OF WOOD OIL ON HEATING. Ger. 274,971 (Oct. 19, 1913); C. A. <u>9</u>, 388 (1915).

"Preventing gelatinization of wood oil upon heating by the addition of a halogen or of compds. and mixts. which readily split off a halogen, such as Cl, Br, I, F, and their readily decomposible compounds. The gaseous halogen or compds. may be led into the cold wood oil and stirred, whereupon the mixt. is heated to a high temp. E. G., wood oil 100 kg. is heated with a soln. of 0.5 kg. Br. in 2 kg. CCl₄, after thorough mixing, to a temp. of 240°. The resulting mixt. remains liquid for hrs. without gelatinizing." From C. A.

Reizenstein, L. J.

PROCESS FOR POLYMERIZING CHINA-WOOD OIL.

U. S. 2,017,164 (Oct. 15, 1935); C. A. 29, 8367 (1935).

"For polymerizing an oil such as China wood oil a stream of the oil is pumped from a supply through a polymerizing zone, is diverted back to the supply and a constant pressure gradient is created on the balance of the oil of about 150 lb. per sq. in., and the oil from the polymerizing zone is discharged back to the supply until the oil leaving the polymerizing zone has attained the desired temp. of about 260-315°, and the heated oil is then passed into a discharge tank. App. is described." From C.A.

Reimann, Ferdinand (to Firm Wilhelm Schmidding, one-half)

DEVICE FOR WORKING WOOD OIL INTO LACQUER.

U. S. 1,864,941 (June 28, 1932); C. A. <u>26</u>, 4487 (1932). "In an app. comprising 3 vessels, raw lacquer substances and wood oil are heated in 2 of the vessels, the inspissation of the wood oil is suitably controlled and the raw lacquer substances are added to the heated wood oil, and the mixing of the materials is completed in the 3rd vessel. Various structural details are described." From C. A. Schmidding, Wilhelm

PROCESS FOR THE PRODUCTION OF WOOD OIL V'RNISHES.

Ger. 522,407 (Feb. 14, 1925).

For the production of wood oil varnish the wood oil is heated in one kettle beneath a second kettle in which resins, etc. are melted. The molten resins are poured quickly into the hot wood oil.

Schmidding, Wilhelm

IMPROVEMENTS IN OR RELATING TO THE PREPARATION OF LACQUERS FROM TUNG OIL.

Brit. 247,599 (Sept. 30, 1926); C. A. 21, 660 (1927).

"Tung oil is thickened without gelatinization by rapid heating to 280-300° and lacquers are formed by running into the thickened oil materials such as resin, resinates, resin' ester, artificial resin, paracoumarone, copal, dammar, oils, fats or fatty acids or mixts. of these. An app. is described." From C. A.

Schmidding, Wilhelm

APPARATUS FOR THE PROCESSING OF WOOD OIL. Ger. 543,906 (Feb. 19, 1927).

An arrangement of 3 kettles; one for heating wood oil, a second one for melting resins and a third in which the hot wood oil and the molten resins are combined.

Schneider, J. L., Flugge, S. L., and Evans, R. J. (to Continental Can Co.) METHOD OF PRODUCING QUICK PRYING OIL SUITABLE FOR VARNISHES.
U. S. 2,120,044 (June 7, 1938); C. A. 32, 6083 (1938). "An oil such as China wood oil is satd. with CO₂ at atm. temp. and pressure, and the oil is forced under a pressure of about 1000 lb. per sq. in. into and through a conduit heated to about 260-370°, and is passed out of the conduit before deleterious carbonization of the oil occurs." From C. A.

Schneider, R. T., Coe, R. H., and Ware, E. E. (to Sherwin-Williams Co.) V/RNISH OIL.

Can. 373,394 (Apr. 26, 1938)*; C. A. 32, 4808 (1938).

"To inhibit gelation during polymerization and to give it the property of forming a nonfrosting film, tung oil is heated to about 400° F., Fe linoleate is incorporated in the proportion not substantially less than 0.5 lb./50 gal. of oil, and the mixt. is heated to higher temp., with stirring, to effect the desired degree of polymerization, cooled, and dild. with a thinning material." From C. A.

Schneider, R. F., Coe, R. H., and Ware, E. E. (to Sherwin-Williams Co.) V/ENISH OIL AND METHOD OF TREATING SAME.

U. S. 2,220,293 (Nov. 5, 1940); C. A. <u>35</u>, 1651 (1941). "A method of treating tung oil to inhibit gelation during polymerization and to give to the oil the quality of forming a nonfrosting relatively fast-drying film consists in heating the oil to about 400° F., then incorporating therein iron linoleate in the proportion of not substantially less than 1/2 lb. to 50 gal. of tung oil, then heating to at least 500° F. while stirring to effect the desired degree of polymerization, and then cooling the oil and adding a thinning material." From C. A. Sommer-Schmidding-Werke Vertriebsgesellschaft

PROCESS AND INSTALLATION FOR THE PREPARATION OF WOOD OIL.

Fr. 763,898 (Feb. 19, 1934); C. A. 28, 5691 (1934).

"Crude wood oil is heated to form stand oil in large amts., e.g. above 100 kg. in a closed vessel contg. an inert gas to about 280° with continual stirring after which cold or moderated heated stand oil from wood oil is added as rapidly as possible and in amt. such that the temp. of the oil in the vessel falls below 200°. If a mixed oil is required stand oil from linseed oil may be added for cooling." From C. A.

Sommer, J., and Ralph, S. J.

PROCESS FOR THE PRODUCTION OF THICKENED OIL WITH ADDITION OF WOOD OIL AND MEANS THEREFOR.

Brit. 362,545 (Dec. 10, 1931); C. A. 27, 1528 (1933).

"Wood oil, heated to near the polymerization point but safely below the gelatinization point is introduced into hot polymerized linseed or like oil in such proportions and dispersion as to be instantly heated to the polymerization point without opportunity for gelatinization, and thoroughly incorporated." From C.A.

Stoddard, W. B., Geiber, H., and Burgess, M. (to Tung Oil Froducts, Inc.) PROCESS OF TREATING TUNG OIL.

U. S. 1,924,524 (Aug. 29, 1933); C. A. 27, 5560 (1933). "The oil is heated in the absence of reaction-retarding diluents and of compds. that combine with the oil, with a small proportion of ZnCl₂ and with a peroxide such as that of acctone until the body of the tung oil has increased, and the treatment is terminated before the oil has coagulated or solidified." From C. A.

"Vernisol" Societe Anonyme, Fabrique de Vernis et Produits Isolants pour L'Industrie Electrique.

> PROCESS FOR PREVENTING THE CELATION OF WOOD OIL ON HEATING. Ger. 253,845 (Apr. 28, 1912); C. A. 7, 713 (1913).

"Preventing gelatinization of wood oil upon heating by b. the wood oil with naphthenic acids contained in the residues from the refining of the lighter petroleums. About 15% naphthenic acids are added to the wood oil, whereupon the product can be heated to 300° and over without gelatinization. The product is a thick and clear oil which does not form a skin or become ropy, dries quickly, and is applicable in the prep. of varnishes." From C. A.

Waldie, W. A.

COLTING COMPOSITIONS.

Brit. 523,525 (July 16, 1940)*; C. A. 35, 6474 (1941).

"A mixt. contg. raw wrinkling oil, resin and a drier is heated until a homogeneous mixt. is produced, quickly chilled without the introduction of cold ingredients, thinned with a solvent to the desired consistency and a pigment incorporated therein. The heat treatment is carried out at 450-550°F. Suitable oils are raw China wood, oiticica and poyak oils. Suitable resins are: Congo, kauri, rosin, Cumar, "Ambercol" copal and phenolformaldehyde resins." From C. A. Waldie, W. A., and Toulmin, H. A., Jr. (to New Wrinkle, Inc.) INFRARED TREATMENT OF OILS.

> U. S. 2,411,767 (Nov. 26, 1946); C. A. <u>41</u>, 1115 (1947). "By infrared irradiation with agitation, tung cil and oiticica oils were bodied in about half the time required for heat-bodying at approx. the same temps. Viscosities are tabulated for the cils infra-red-treated and heat-bodied for 1-9 hrs." From C. A.

Ward, J. P. (to General Coating Co.)

APPARATUS FOR BODYING TUNG OIL.

U. S. 2,090,586 (Aug. 17, 1937); C. A. <u>31</u>, 7273 (1937).

"An app. is employed having walls defining upper and lower compartments, means defining an oil-treating chemical channel in each of the compartments terminating short of the top of such compartment, means for supplying oil continuously to the upper channel, the lower channel being of a size similar to the upper, conduit means connecting the channels for passage of liquid only from the upper to the lower thereof, means for maintaining and renewing an atm. of gas above the oil in each of the channels, and means for maintaining progressively higher temps. in succeeding portions of the upper channel and a substantially const. temp. in the lower channel." From C. A.

Weinschenck, Arthur

TREATMENT OF WOOD-OIL.

Ger. 219,715 (July 21, 1909); C. A. 4, 2211 (1910).

"In the treatment of wood-oil to prevent the coagulation at higher temps., ord. crude wood-oil is heated up to 90-200° with a pulverulent, strongly reducing metal, such as Zu dust. The treated oil can without danger of coagulation be heated to 200-40°. While the product takes longer to dry than the crude oil, yet its drying properties are recovered by the addition of drying substances or siccatives." From C. A.

Williams, E. M.

PROCESS FOR MANUF CTURE OF MISCIBLE GUM FROM DRYING OILS.

U. S. 2,082,371 (June 1, 1937); C. A. <u>31</u>, 5606 (1937). "A gum which is suitable for use in paints, varnishes, etc., is obtained by heating a quantity of China wood oil with a greater quantity of menhaden oil at a temp. of approx. 205°, adding a quantity of Pb and Co acetates at said temp. and zerating the mixt. to produce a thickened oil mixt., adding a quantity of linseed oil and China wood oil, to said heavy-bodied oil, heating the same at a temp. of approx. 205°, adding up to 5% of Pb acetate, cobalt acetate and calcined MgO at such temp. and processing the same to a gum." From C. A. Winkler, K.

PROCESS FOR THE MANUFACTURE OF RAPIDLY DRYING MASSES, SUITABLE FOR PROTECTIVE AND INSULATING COVERINGS AND IMPREGNATIONS. Gcr. 247,373 (Aug. 28, 1910); C. A. 6, 2550 (1912).

A process for the production of rapidly drying masses, suitable for protective and insulating coatings which consists in heating oils and fats with phenol and, if desired, with driers and solvents. It may be done under reflux or under pressure. The inflammability may be reduced by incorporating bound nitrogen into them by heating with 5% of dried, ground leguminous seeds and filtering. In an example, china wood oil (90 parts), crude phenol (30-170) and castor cil (5) are heated under pressure at 300° C. until the mass attains the consistency of honey.

Winkler, K.

PROCESS FOR THE FREPARATION OF RAPID DRYING MASSES, SUITABLE FOR PROTECTIVE AND INSULATING COATINGS AND IMPREGNATIONS. Ger. 252,139 (Aug. 28, 1910).

Rapidly drying masses, suitable for protective and insulating coatings and impregnations can be prepared by heating oils and fats with amorphous phosphorous to temperatures above 150° and, if desired, with driers and diluents. Additions of phenol improve the products. Drying oils, especially Chinese wood oil, bankulnut oil, and safflower seed, are suitable. Example: Chinese wood oil (90), castor oil (5) and amorphous P are hested under pressure at 220° until the mass attains the consistency of honey.

Wirth, Robert, Wolf, O. R., and Kohler, A.

PROCESS AND APPARATUS FOR THICKENING WOOD OIL.

Brit. 364,516 (Jan. 7, 1932); C. A. 27, 2050 (1933).

"In thickening wood oil by heat, the oil is pumped continuously through a heater to a collecting vessel, from which it falls continuously at the same rate to a cooler, the conditions being such that it leaves the heater at 260-80° and is in the vessel just long enough to raise its temp. about 20° by polymerization. App. is described." From C. A. IX. MODIFICATION OF TUNG OIL BY CHEMICAL TREATMENT

Bakelite Corp.

PROCESS FOR THE MANUFACTURE OF HARDENABLE RESINOUS COMPOSITIONS. Fr. 700,063 (Dec. 22, 1930); C. A. 25, 3503 (1931).

"Hardenable resinous compns. are made by the reaction of FhOH and wood oil in the presence of a small quantity, e.g., 1-2%, of H₂PO, as accelerator. An aq. soln. of CH₂O or other hardening agent contg. CH₂ is added in amt. to form products capable of hardening and org. solvent of medium or high b.p. which prevents gelatinization e.g., BuOH or AmOH. The water is eliminated as a const.-boiling mixt. at a temp. below 120° by the addn. of toluene." From U. A.

Baldwin, J. T.

PROCESS OF PRODUCING AN OXIDIZED OIL GEL.

U. S. 1,971,634 (Aug. 28, 1934); C. A. 28,6580 (1934).

"A highly oxidized oil is produced by subjecting to pressure a dispersion of an oil gel such as one from linseed or China wood oil in a volatile dispersing medium such as CCl₄, and introducing O into the dispersed gel." From C. A.

Bellefontaine, A., Bernard, H., and Sieberg, A.

RESINOUS MATERIALS.

U. S. 2,285,797 (June 9, 1942); C. A. 36, 7336 (1942).

"A drying oil such as Chine-wood oil, an oil-compatible natural resin such as colophony or an oil compatible synthotic resin is heated (suitably to about 150-300°) in admixt. with a polynuclear polyhydric phenol in which at least one H atom of each of at least 2 different hydroxaryl radicals thereof is replaced by an allyl or a crotyl radical, such as diallyldihydroxydiphenyldimethylmethane or a sol. and fusible polymerization product of such a phenol." From C. A.

Blakeman, W. N.

DRYING OIL.

U. S. 767,682 (Aug. 16, 1904).

Drying oils can be prepared by mixing 15 parts of tung oil with 85 parts of non-drying fatty oil (e.g., cotton-oil). Either the tung oil or the non-drying oil, or both, may be oxidized before being combined.

Blakeman, W. N.

OIL AND PROCESS OF MAKING SAME

U. S. 792,113 (June 13, 1905).

The drying and spreading behavior of fatty oils and their mixtures can be improved by elaidinizing one or all of the oils. They may be exidized either before or after elaidinizing. The latter process can be effected by exides or acids of nitrogen, preferably nitrous acid or the red fumes of fuming nitric acid. Treated oils that are slow to dry can be improved by adding fast drying cils such as tung or linseed. Oils treated with exides of nitrogen include olive, castor, cotton, sunflower, ben or sesame, linseed, tung and rosin oils. In an example, fully elaidinized linseed oil (10), partially elaidinized cotton-oil (75) is fortified with tung oil (15) yielding an economical and satisfactory vehicle.

PAINT AND PROCESS OF MAKING S.ME.

U. S. 792,114 (June 13, 1905).

This patent covers the manufacture of paints by combining pigments with the oils described in U. S. patent 792,113. Elaidinized olive, castor, cottonseed, sesame,linseed, tung or rosin oils may be blended with fast drying oils such as tung or linseed and then ground with white lead, lead oxysulfate or sublined lead, PbSO, BaSO, BaCO, CaCO, SrCO, SrSO, etc. An example specifies fully claidinized cotton oil (10); partially elaidinized cotton oil (75) and tung oil (15) with ZnO (100) or FbSO, (240) or ZnO (30), FbSOL (30) and BaSO, (30).

Blakeman, W. N.

PAINT COMFOUND.

U. S. 883,513 (Mar. 31, 1908).

The inventor claims the compound or mixture of a pigment deficient in spreading power with a hydrated fatty oil, a hydrated drying fatty oil or an oxidized and hydrated oil. Hydration may be effected by storing the oil in open vessels in a damp atmosphere or by agitating oil in which .04 - .05% H₂O has been dispersed. Commercial linseed, tung or other oils, animal or vegetable, hydrated by this process will show the presence of hydrated acids not found in fresh oil. The hydrated oil will add spreading power to FbSO₄, FbSO₅, FbCO₅ (anhydrous), sublimed lead, ZnO, ZnS, BaSO₄, BaCO₅, CaCO₅, SrSO₁, SrCO₅, etc. Example: 100 parts of linseed oil hydrated with 0.04% H₂O combined with 240 parts of FbSO₁, containing 1% of Zn(OH)₂.

Blakeman, W. N.

FAINT COMPOUND AND PROCESS OF MAKING THE SAME.

U. S. Pat. 883,514 (Mar. 31, 1908).

Figments deficient in spreading power give satisfactory paints with hydrated oils such as tung oil, linseed oil, etc. Claim 1 applies to "a compound or mixture of a fatty oil, a hydrated fatty agent; and a pigment which contains no hydroxyl and is deficient in spreading power." Claims 3 and 4 specify hydrated tung oil and claim 5 applies to the process described.

Blakeman, W. N.

OIL.

U. S. 883,515 (Mar. 31, 1908).

Hydrated oils improve the spreading character of hydroxyl-free pigments when the latter are used in paints. Claim 1 applies to a compound or mixture of a drying fatty oil and a hydrated fatty agent. Claim 3 specifies a compound or mixture of linseed oil and hydrated tung oil.

FIGMENT COMFOUND AND PROCESS OF MAKING THE SAME.

U. S. 883,516 (March 31, 1908).

A paste, which, when diluted, makes a paint, is composed of a pigment deficient in spreading power and hydrated fatty oil. Tung oil, linseed oil, castor oil, olein, stearin, or oleic acid can be used if hydrated by agitation at 140° with 2-3% of water for 20-25 hrs.

Blakeman, W. N.

FAINT COMFOUND AND PROCESS OF MAKING THE SAME.

U. S. 883,518 (Mar. 31, 1908).

The claims cover a paint composed of a fatty oil, a rancidified agent and a pigment deficient in spreading power together with the process of making such a paint. Linseed cil is preferred though tung, castor or other oil may be used. The rancidified agent is an oil which has been hydrated and oxidized.

Blakeman, N. N.

PAINT COMPOUND AND . ROCESS OF MAKING THE SAME.

U. S. 883, 520 (Mar. 31, 1908); C. A. 2, 2457.

There is claimed "A compound or mixture, in paste form, of a pigment which contains no hydroxyl and is deficient in spreading power and a rancidified fatty substance." The latter is preferably formed from linseed oil, but can be made from tung oil, castor oil, oloin, stearin, oleic acid or similar substance.

Blakeman, W. N.

OIL.

U. S. 883,521 (Mar. 31, 1908); C. A. 2, 2457 (1908). "Hydrated tung oil, a drier and a pigmont." From C. A.

Blakeman, W. N.

OIL. U. S. 883,522 (Mar. 31, 1908); C. A. 2, 2457 (1908). "A rancidified hydrated tung oil and linseed oil with a drier." From C. A.

Blakeman, W. N.

IMFROVEMENT IN THE MANUFACTURE OF FAINT COMFOUNDS. Fr. 388,736 (issued June 6, 1908). Similar to Brit. 7090 (1908). The claims cover the use of hydrated oils (such as tung or linseed oils), a process of hydrating oil and the products (paints) that are obtained.

Blakeman, W. N.

IMFROVEMENT IN THE MANUFACTURE OF FAINT COMPOUNDS.

Fr. 388,737 (June 6, 1908).

This Fronch specification is substantially the same as Brit. 7100 (1908). The claims pertain (1) to the use in paint compounds of an oil or other fatty matter that has been randdified, (2) to the use of rancidified oil with another oil, (3) to the use of rancidified oil with pigments and (4) to the products of the above uses. Recommended oils are linseed and abrasin (tung).

IMFROVEMENT IN OILS USED FOR PAINTING.

Fr. 389,369 (June 26, 1908)

This specification is substantially the same as U.S. 883,522 (1908) and Brit. 7110 (1908). There are 3 claims, as follows: (1) Hydrated or rancidified abrasin oil (also known as tung and Chinese wood oil); (2) a compound of rancidified abrasin oil and another oil, with or without a drier: (3) a compound of rancidified abrasin oil and a hydrated oil.

Blakeman, M.N.

INPPOVEMENT IN OILS USED IN PAINTING. Fr. 389,769 (July 9, 1908).

This patent covers a new industrial product consisting of abresin oil (also known as tung oil and Chinese wood oil) having water chemically combined with it, and mixtures of hydrated abrasin oil with the other oils. This is similar to U.S. 883,521 (1908) and Brit. 7103 (1908).

Blakeman, W.N.

INPROVEMENTS IN THE MANUFACTURE OF PAINT COMPOUNDS,

Brit, 7,100 (1908) (Sept. 3, 1908); C.A. 3, 1218 (1910).

The use of a rancidified oil, such as a treated tung oil or linseed oil, permits the use in paints of pigments which are normally deficient in spreading power. Rancidification is effected by exposing the oil to air and light in shallow vessels. This patent applies to the use of rancidified oils, especially in paints, and to the products obtained.

Blakoman, W.N.

INPPOVEMENTS IN AND RELATING TO OILS,

Brit. 7, 110 (1908) (Sept. 3, 1908); C.A. 3, 1218 (1909)
 "A quick-drying oil, composed of a mixture of rancified tung
 oil (Chinese wood oil), and another oil, with or without a dryer."
From C.A.

Blakeman, W.N.

INTPOVEMENT IN THE MANUFACTURE OF PAINT COMPOUNDS

Brit. 7090 (1908) (Sept. 10, 1908); C.A. 3, 1346 (1909)

"In the manufacture of paint compounds the use of a hydrated oil or other hydrated fatty substances with or without the addition of other cils." From C.A. This specification is similar to French Patent 383,736

This specification is similar to French Patent 383,736 (Blakeman, 1908). Although other fatty products may be used, either linseed or tung oil is preferred.

Blakeman, W.N.

INPROVEMENTS IN AND RULATING TO OILS.

Brit. 7103 (1908) (Sept. 10, 1908): C.A. 3, 1348 (1909) "As a new composition of matter, tung oil having water chemically combined therewith." From C.A.

OIL AND COMPOUND THEREOF.

U.S. 989,226 (Apr. 11, 1911); C.A. 5, 2190 (1911)

"Composition for a paint vehicle, consisting of chlorinated tung oil and a non-drying fatty oil. Chlorinated cotton oil, sunflower oil, linseed oil, poppy oil, hemp oil, corn oil and rosin oil may also be used in various mixtures." From C.A.

Blakeman, W.N.

INTROVEMENTS IN INDUSTRIAL OILS, FATS AND COMPOUNDS THEREOF. Fr. 428,499 (June 22, 1911)

This French specification is very similar to British Patent 9027 (1911). Claim 2 covers a compound of a fatty oil, either drying or non-drying and chlorinated wood oil. Claim 4 refers to the use of this compound with pigments for the manufacture of paints.

Blakeman, W.N.

IMPROVEMENTS IN OILS AND COMPOUNDS THEREOF. Brit. 9027 (1911) (Apr. 11, 1912); C.A. <u>6</u>, 2855 (1912) "Fatty oils and fats, etc., are chlorinated and used, with or without the addition of a drying oil (preferably tung oil) or a com. drier, or both, as vehicles for paint pigments. Instead of chlorinating the whole of the vehicle, a proportion of a chlorinated agent may be mixed with the ordinary vehicle, which may also be slightly chlorinated. The chlorinated oil or fat, etc., may be oxidized." From C.A.

Clayton, E.C., and Heffner, L.L. (to Wm. E. Hooper & Sons Co.) PAINTING AND SIMILAR COMPOSITIONS.

U.S. 2,118,787 (May 24, 1938); C.A. <u>32</u>, 5647 (1938)

"A compn. is used which may comprise substantially 27% of approx. 60% chlorinated org. compd. selected from the group consisting of chlorinated paraffin; chlorinated rubber; chlorinated vinyl resin; chlorinated neutral oil; chlorinated straw-colored petroleum oil; chlorinated tung oil; chlorinated castor oil; chlorinated soybean oil; and chlorinated fish oil; a solvent of the chlorinated material which is released by evapn. at normal temps., and approx. 5 to 20% of a salt in solid finely divided form, selected from the group consisting of Zn borate, Mg borate, manganous borate and manganese borate, a pigment, and filler, the solvent being in sufficient proportions to make the compn. capable of application by brushing, dipping or spraying." From C.A. INPROVEMENTS IN OR RELATING TO THE MANUFACTURE OF MINTD ESTERS OF POLYHYDPIC ALCOHOLS AND RESINS AND COATING COMPOSITIONS MANUFACTURED THEREFROM

Brit. 405,827 (Feb. 15, 1934); C.A. 28, 4924 (1934)

"Fatty oils are prepd. by alcoholysis of a frosting or nonfrosting oil with a polyhydric alc, followed by esterification of the product with fatty acids derived from a non-frosting or frosting oil, resp. The oils produced may contain free alc. groups or may be treated with a further quantity of polyhydric alc. Esterification catalysts, e.g., oxide of Pb, Na, Ca, Ba, Zn, cr Mg, may be used. China-wood, Japanese-wood and oiticia oils are frosting oils, i.e., they dry to a flat opaque film, and any other fatty oil, including drying, semi-drying or nondrying oils such as linseed, safflower, sun-flower seed, perilla, soy bean, rubber seed, cottonseed and sardine oils, may be used as the non-frosting oil. Suitable alcs. are glycerol, sorbitol or pentaerythritol. The oils may be used in the manuf. of coating compns, and especially those contg. free OH groups, for the manuf, of alkyd resins. In examples (1) China-wood or linseed oil, glycerol and PbO are heated together and the product is heated with linseed or China-wood oil fatty acids, resp., to yield a neutral oil, (2) a varnish is prepd, comprising the oil of (1) ester gum, mineral spirits and a Co drier and (3) and alkyd resin is prepd, by heating a synthetic China-wood linseed oil, glycerol and linseed oil together and treating the product with phthalic anhydride. The product dissolved in a thinner with a drier, yields a varnish." From C.A.

Ellis, Carleton

TROCESS OF MAKING EDIBLE OILS, ETC.

U.S. 1,052,469 (Feb. 11,1913) C.A. 7, 1302 (1913)

"Hydrogenating oils, etc., by passing a stream of the material slowly through a porous bed of catalytic comp. e.g., nickelized pumice, moving transversely to the direction of the stream, and simultaneously bringing a counter-current of H into contact with the material. A temp. of about 150-175° is maintained." From C_0A_0

The process is said to be applicable to China wood oil.

Ellis, Carleton.

COATING COMPOSITION

U.S. 1,189,550 (July 4, 1916); C.A. 10, 2136 (1916) "Vulcanized Chinese wood oil is mixed with Jelutong or Pontianak resin, a thinner such as C6H6 and gasoline and, if desired, with rubber, vulcanized cottonseed oil, tar, gilsonite or pigments." From C.A.

Groff, Frazier (to Union Carbide and Carbon Corp.) POLYVINYL PARTIAL ACETAL COMPOSITION AND METHOD OF MAKING THE SAME. U.S. 2,533,314 (Dec. 12, 1950); Pelyvinyl partial acetal resins are rendered soluble in fatty drying oils and compatible with the usual ingredients of filmforming compositions by heating the resins with a water insoluble monocarboxylic acid containing at least 10 carbon atoms to the molecule and preferable in the presence of a drying oil such as linseed or tung. In one example, a varnish is prepared by heating polyvinyl partial butyral resin (37.5 parts) with resin (5 parts) at 260°C. until the reaction product is clear when cold. China-wood oil (25 parts) is added and the composition heated at 270°C. for about 1/2 hr. yielding a clear viscous liquid when hot and a clear, tough, gum-like product when cold.

Horn, A.C.

PLASTIC WATER-PROOFING COMPOSITION.

U.S. 1,149,519 (Aug. 10, 1915);* C.A. <u>9</u>, 2715 (1915) "A plastic composition for waterproofing walls, etc., is formed of mineral filler or pigment mixed with Chinese wood oil which has been slightly vulcanized by heating to 205° with about 3% its wt. of S." From C.A.

I.G. Farbonindustrie, A.-G.

PROCESS FOR THE PRODUCTION OF OXIDATION PRODUCTS OF DRYING OILS. Ger. 472,111 (Aug. 12, 1924); C.A. 23, 2584 (1929)

"Drying oils are troated with air or O while suspended in a liquid in which they are insol., e_0g_0 , in water, aq_0 solns, of org. acids, alcohols, etc. Colloids, e_0g_0 , gelatin, may be added to prevent coagulation of the oxidized oil, and accelerators, e_0g_0 , compds. of Pb, Mn or Co, may be present also. Examples are given." From C_0A_0

The raw material used may be either linseed oil, tung oil, soybean oil or fish oil, and either crude, refined or boiled.

I.G. Farbenindustrie, A.-G. (Rosenthal, L., and Kropp, W.)

PROCESS FOR THE PRODUCTION OF BOILED WOOD OIL AND WOOD-OIL VARNISHES.

Ger, 516,369 (Dec. 1, 1926); C.A. <u>26</u>, 4725-6 (1932) "Wood oil or a varnish contg. wood oil is treated with a small amt. of an aralkylated phenol, e.g., 1-benzyl-2-naphthol. Clear, lustrous products showing no tendency to form a skin are obtained. Examples are given." From C.A.

I.G. Farbenindustrie, A.-G.

PROCESS FOR THE PRODUCTION OF HIGH-GRADE "OOD OIL. Ger. 529,077 (Oct. 27, 1929); C.A. 25, 5048 (1931).

"The tendency of wood oil to gelatinize is greatly reduced by incorporation of hydroxy-or polyhydroxyalkyl esters of fatty acids contg. at least 12 C atoms in the mol. Such esters are obtainable by the reaction of the acids with an alkylene oxide or an excess of a glycol. Esters of the fatty acids of wood oil are preferred. Thus, wood oil 1000 may be mixed with hydroxyethyl esters of wood oil acids 300 parts. If the oil has a high acid value neutralization of the oil with an alkylene oxide may suffice." From C. A. Koenig, W.J.

COMPOSITION OF MATTER AND NETHOD OF MAKING THE SAME, U.S. 2,058,596 (Oct. 27, 1936); C.A. <u>31</u>, 280 (1937) "Drying oils such as blown Chinawood cil used for coatings or plastics are hardened by heating them with an oxy-cyclic org. compd. such as cyclohexanone (suitably at a temp. of about 175°.)" From C.A.

Koenig, W.J. (to Sloane-Blabon Corp.)

COMPOSITION OF MATTER AND METHOD OF MAKING THE SAME U.S. 2,135,976 (Nov. 8, 1938); C.A. <u>33</u>, 1525 (1939)

By a treatment such as heating together for 5 hrs., a condensation reaction is effected between an oxidized drying oil (such as blown China-wood oil) having double bonds in conjugate arrangement and a straight-chain alc. contg. 6 or more C atoms, a straight-chain satd. aldehyde contg. 3 or more C atoms, a straight-chain ketone contg. 5 or more C atoms or a straight-chain unsatd. hydrocarbon contg. 6 or more C atoms (by use of geraniol, butyraldehyde, mesityl oxide or diiso-butylene).

Lilienfeld, L.

INPROVED NANUFACTURE OF PLASTIC SUBSTANCES. Brit, 15,657 (1912) (Dec. 19, 1912); addn. to 636 (1910); C.A.<u>8</u>, 265 (1914).

"In the manuf. of plastic materials, the resinous products obtained according to the principal patent, 636,(1910), from Chinese wood oil, wood oil fatty acids, or their derivs. are treated with HCHO, or are produced in the presence of HCHO. The process may be carried out under neutral, acid, or alk. conditions and the HCHO may be in gaseous form or in soln." From C.A.

Meusel, E.

PROCESS FOR TRANSFORMING FATTY OILS BY MEANS OF BACTERIA Ger. 149,822 (Mar. 11, 1903)

Fatty oils are treated with denitrificating bacteria in the presence of nitrites or nitrates, other nutritive salts and air. Linseed, colza, olive, poppy, cottonseed, palm, coconut, hemp, and wood oils are oxidized causing a reduction of iodine no. but not of saponification no. If these oxidized oils are further oxidized with dilute HNO3, they yield products useful as mordants in the dyeing of cotton.

Neusel, Eduard

INPROVEMENTS IN AND RELATING TO THE MANUFLCTURE OF OILS. Brit. 7410 (1903) (June 11, 1903)

"The production of chemically modified oils, which consists in subjecting fatty oils to the action of bacteria in the presence of nitrates or nitritos or nutritive salts, the mixture being well aired throughout the period of reaction, substantially as and for the purpose herein set forth." Claim No. 1 of the patent. Meusel, Eduard

PROCESS FOR THE MANUFACTURE OF OILS MODIFIED BY DECAY AND THEIR PREPARATION FOR INDUSTRIAL USES,

Fr. 330,389 (June 26, 1903)

Similar to British Patent 7410 (1903) by the same inventor.

Mcusel, Eduard

PROCESS OF CHEMICALLY MODIFYING OILS.

U.S. 794,373 (July 11, 1905).

Fatty oils are modified by mixing the oils with aqueous solutions of nitrates and subjecting them to denitrificating bacteria which cause the glycerine and oleic acids of such oils to be oxidized. Products suitable for industrial uses can be made from linseed, castor, colza, olive, poppy, cotton, palm, cocoanut, hemp, and wood oils.

New Wrinkle, Inc.

PPOCESS FOR INCREASING THE VISCOSITY OF A DRYING VEGETABLE OIL. OIL THUS TREATED,

Swed. 120,672 (Nov. 4, 1946); (Jan. 20, 1948);* Peintures, pigments, vernis 25, (2), 64 (1949) (abstract)*; Oleagineux 4, (4), 265 (1949)

"Action of infrared light on China wood oil or oiticica oil." Translated from Oleagineux.

Nichols, 'oseph (to Interchemical Corp.)

. .

MODIFIED DRYING OIL.

U.S. 2,497,904 (Feb. 21, 1950); ^J. Am. Oil Chemists' Soc. <u>27</u>, 152 (1950)

"The drying qualities of tung oil are improved by refluxing the oil with acetic anhydride at 160-180° and removing the anhydride." From J. Am. Oil Chemists' Soc.

Root, F.B. (to Ellis-Foster Co.)

COMPOSITION FOR COATING PURPOSES CONTAINING A RUBBER DERIVATIVE. U.S. 2,068,818 (Jan. 26, 1937); C.A. <u>31</u>, 2030 (1937)

A compn. suitable for coating metals, wood, etc., contains chlorinated rubber together with tung oil sulfurized by heating with not more then about 1% of S.

Scheiber, Johannes

PROCESS FOR THE MANUFACTURE OF VARNISH PRODUCTS OF ALL KINDS FROM WOOD OIL

Ger. 511,044. (July 31, 1928); C.A. 25, 1400 (1931)

"Wood oil for use in making varnishes, etc., is treated with the amt. of H or Cl required to sat. one of its double bonds. The hydrogenation may be effected at 180° in the presence of Ni as a catalyst. The chlorination may be effected during cooling. Examples are given." From C.A. Scobel, Benjamin

PROCESS OF PRODUCING SOLIDIFICATION OF OLEAGINOUS SUBSTANCES. Brit. 153,942 (Nov. 5, 1920); C.A. 15, 1082-3 (1921)

"Tung oil or Chinese wood cil is solidified by the action of halide salts, particularly chlorides, uniformly disseminated through the oil. To secure this dissemination, the chlorides are first ground up with an indifferent oil, such as resin oil or linseed oil, or dissolved in an anhydrous org. solvent, and the liquid produced is mixed with the tung oil. Suitable combinations of salts and solvents are anhydrous FeCla in anhydrous acetone, anhydrous AlCl₃ in anhydrous acetone, anhydrous SnCl₂ in acetone, anhydrous ZnCl₂ in acetone or amyl alc., and Sb or Bi chloride in acetone; the use of FeBr₃ is also mentioned, and mixts, of various salts may be employed. Fuming chloride may be dissolved in benzine or the like and mixed with an indifferent oil and the mixt, added to the tung oil, or they may be changed into hydrated chloride and dissolved in anhydrous solvent and used directly, Filling and coloring matters, fibrous or otherwise, may also be added; a number of suitable and unsuitable substances are mentioned. Rosin gums, ester gums, or other gums easily sol. in oil may be added to the tung oil, as may tung oil fatty acids. Either raw or blown tung oil may be employed, but oil that has been partly polymerized by heat is unsuitable," From C.A.

Scobel, Benjamin

PROCESS FOR SOLIDIFYING CHIMA-WOOD OIL AND THE PRODUCT THEREOF. U.S. 1,383,864 (July 5, 1921)*; C.A. 15, 3758 (1921)

"Chinawood oil is thoroughly mixed with FeCl₃,ZnCl₂, AlCl₃, or similar halides previously ground in rosin oil or linseed oil to form a moldable mixt., which is seasoned by gentle heating." From C.A.

Seigle, ".R.

METHOD OF MODIFYING OILS AND THE PPODUCT THEREOF. U.S. 1,436,362 (Nov. 21, 1922): C.A. <u>17</u>, 618 (1923)

"Tung oil is partially hydrogenated, gilsonite is dissolved in the oil and the mixt, is then heated to effect polymerization and render the product suitable for use with fiber in the manuf. of brake linings or other articles." From C_0A_0

Shechter, Leon, and Whelan, J.M. (to Union Carbide and Carbon Corp.) KETENE-ALDEHYDE MODIFIED OILS.

U.S. 2,534,306 (Dec. 19, 1950).

Upgrading of soft drying oils is accomplished by preparing nixed esters of the oils, their acids or partial polyhydric alcohol esters of the acids with a C-C linkage reaction product of ketene with an unsaturated aldehyde. Improvement of tung and oiticica oils is claimed. Acids which may be used include lauric, myristic, palmitic, stearic, linoleic, oleic, eleostearic, licanic, ricinoleic, clupadonic, etc. VARMISH PAINT OR WATERPROOFING COMPOSITION AND PROCESS FOR MAKING SAME.

U.S. 1,464,224 (Aug. 7, 1923)

J. Soc. Chem. Ind., <u>42</u>, 1032A (1923)

"An unsaturated vegetable oil, such as tung oil, is treated with a small proportion of phosphorus pentoxide, whereupon polymerisation to a gelatinous waterproof substance commences. The mixture is immediately added to a solution of a rosin, such as coumarone resin ("cunar"), in linseed oil, and polymerisation is completed by heating and allouing to stand. The composition may be used as a base for varnishes, paints, or waterproofing materials. The products are distinguished by their rosistance to weather." From J. Soc. Chem. Ind.

X. COATINGS (a) Tung Oil-Modified Alkyd Resins

Allgemeine Elektriciatats-Gesellschaft

PROCESS FOR THE PRODUCTION OF A SYNTHETIC RESIN BY CONDENSAT-ION OF A POLYHYDRIC ALCOHOL WITH A POLYBASIC ACID OR WITH ITS ANHYDRIDE,

Ger. 547,963 (May 23, 1926); C.A. 26, 3687 (1932)

"Polyhydric alcs. are condensed with polybasic acids or their anhydrides with admixture of a small quantity of H_2SO_4 , and, optionally, a fatty acid such as linoleic or eleostearic acids. Thus, glycol or sorbitol is condensed with phthalic anhydride or camphoric acid." From C.A.

American Cyanamid Co. (Bradley, T.F.)

IMPROVEDENTS IN POLYHYDRIC ALCOHOL-POLYBASIC ACID RESINS. Brit. 395,899 (July 27, 1933); C.A. 28, 665 (1934)

"The fatty acids of walnut oil, with or without walnut oil and other oils and fatty acids, e.g., linseed or tung oils, heat treated if desired, are condensed with a polybasic acid or anhydride, e.g., phthalic anhydride, and a polyhydric alc., e.g., glycerol, to give a resincus product." From C.A.

American Cyanamid Co. (Bradley, T.F.)

DEXING OIL COMPOSITIONS AND IMPROVED POLYHYDRIC ALCOHOL-POLYBASIC ACID RESINS PREPARED THERE ITH.

Brit. 412,558 (June 25, 1934); C.A. 28, 7561 (1934)

"A modified drying oil is prepd. by mixing raw tung oil with a higher fatty acid and (or) a resin acid and heating to yield a product having an acid no. of at least 100. The product may be caused to react with 1 or more polyhydric alcs. and 1 or more polybasic acids, or anhydrides thereof, to yield a resin. Among 'examples, tung oil is heated with tung oil fatty acids to give a product the NH, deriv. of which is a soap and the Ca deriv. a resinous substance. Other oils or fatty acids may be added before heating." From C.A.

Baird, William, and Walker, E.E. (to Imperial Chemical Industries, Inc.) MANUFACTURE OF RESINS PRIMARILY OBTAINED FROM POLYHYDRIC AL-COHOLS AND POLYBASIC ACIDS.

U.S. 1,925,947 (Sept. 5, 1933); C.A. 27, 5562 (1933)

"Materials such as glycerol, phthalic anhydride and castor oil are heated together and the resulting reaction mixt, is then further heated with a non-hydroxylated oil such as tung oil or linseed oil until resinification is effected. The product thus formed is of soft resinous character and may be used in varnishes, etc." From C.A.

British-Thomson- Houston Co., Ltd.

RESINOUS COMPOSITIONS,

Brit. 235,595 (June 13, 1924);* C.A. 20, 997 (1926) "Complex ester resins such as those produced from glycerol and phthalic acid or phthalic anhydride are blended with China wood oil, linseed oil, soy bean oil, cottonseed oil, castor oil or other drying, semi-drying or non-drying oils and heated to make varnish or japan compns. in the presence of a nonvolatile solvent, such as benzyl benzoate, benzyl acetate, $PhNO_2$, toluidine, benzyl alc., cresol, aniline, glycol diacetate, phenylhydrazine, or o-cresyl benzoate. The resin oil blend may be freed from the solvent initially used and subsequently dissolved in a volatile solvent such as solvent naphtha." From C_oA_o

British-Thomson-Houston Co. (Adams, L.V.)

IMPROVEMENTS IN AND RELATING TO PAINTS,

Brit. 337,682 (Nov. 6, 1930): C.A. 25, 2310 (1931)

"Metal powders such as Al, Zn, Cu alloys (bronzes), Ag. and Au are suspended in a solution comprising a volatile solvent and a synthetic resin compn. such as one formed from glycerol, phthalic achydride, linseed oil fatty acids, wood oil, resin and dicthylene glycol. Paints thus formed contg. Zn or Al may be applied to base metals such as iron or Cu and the Zn or Al subsequently alloyed with the coated base metal surface by heating." From C.A.

British-Thomson-Houston Co., Ltd. (Durant, W.W.)

INPROVEMENT IN AND RELATING TO COATING COMPOSITIONS

Brit. 343,624, (Feb. 26, 1931); C.A. 25, 4423 (1931).

"A polyhydric alc, such as glycerol is heated with a polybasic acid or its anhydride such as phthalic anhydride, a dryingcil acid such as acids of linseed oil, a natural resin such as rosin and a nondrying oil such as castor oil, with or without a drying oil such as linseed or China wood oil, to a reaction temp. of about 240-60° to produce a fusible and sol. resinous product (preferably with an acid no. less than 25) which can be converted into an infusible and insol. state by further heating and oxidation. Solvents such as diethylene glycol and coal-tar naphtha may be used in preps, insulating compns., etc." From C.A.

British-Thomson-houston Co, Ltd. (Schlingman, P.F.)

IMPROVEMENTS IN AND RELATING TO RESINCUS CONDENSATION PRODUCTS. Brit. 370,440 (Apr. 5, 1932); C.A. 27, 3096 (1933)

"Resins contg. any desired proportion of drying or semidrying oil chemically combined are made by adding the oil slowly to heated phthalic anhydride (or other acid ingredient of an alkyd resin) with or without a natural resin and, when all the oil is combined, adding the glycerol or other polyhydric alc., with further heating, to the desired stage of condensation. In examples there are used linseed, China wood, castor and cottonseed oils, glycerol and glycol, rosin and copal." From C.A.

British-Thomson-Houston Co., Ltd.

POLYHYDRIC ALCOHOL-POLYBASIC ACID CONDENSATION PRODUCTS. Brit. 468,542 (July 7, 1937)*; C.A. 32, 815 (1938) "Shellac (I) is incorporated in the mole of an alkyd resin by causing the reaction in stages of I, a polybasic acid (II), e.g., phthalic or maleic anhydride, succinic, sebacic, adipic or citric acid, a polyhydric alc. (III), e.g., glycerol, ethylene-glycol, butyleneglycol, diethyleneglycol, pentaerythritol, a fatty oil acid (IV), e.g., linseed, chinawood, soybean, cottonseed, sunflower, fish oil fatty acids, stearic or oleic acid, or a natural resin acid (V), e.g., abietic acid, pine tar oil acids, and, if desired, a fatty oil (VI), e.g., soybean oil." From C_cA_o

Bruson, H.A., and Niederhauser, W.D. (to Resinous Products & Chemical Co.) HIGH MOLECULAR-VEICHT GLYCOLS.

U.S. 2,415,335 (Feb. 4, 1947); C.A. <u>41</u>, 3117 (1947) "Glycols of the general formula, $C_2H_9R(CH_2OH)R'CH_2OH$, in which h is a 6-membered alicyclic hydrocarbon group and R' is a divalent straight-chained hydrocarbon group of 9 C atoms, are obtained by hydrogenation of the addn. products of an ester of acrylic acid and of eleostearic acid in the presence of a Cu chromite catalyst and subsequent reduction of the ester groups of the adduct. These glyc is are useful in the prepn. of linear polyesters and alkyd resins of both the drying and nondrying types." From C.A.

Burns, Robert, and Imperial Chemical Industries, Ltd.

PROCESS FOR THE MANUFACTURE OF NEW RESIN-LIKE PRODUCTS FROM POLYBASIC ACIDS AND POLYHYDROXY COMPOUNDS,

Brit. 408,597 (Apr. 6, 1934); C.A. 28, 5692 (1934)

"Resins are prepd. by reacting hexahydroxycyclohenane, or the mono or di-methyl ether thereof with one or more polybasic acids or anhydrides thereof in the presence or absence of modifying agents, e.g., (semi)drying oils, non-drying oils, natural resins or their corresponding acids or other monobasic acids. The reaction may take place in the presence of solvents, e.g., tetrahydronaphthalene (I), entraining liquids, e.g., xylene, or known esterification catalysts, e.g. H3FO4, Ca glycerate, PbO, Suitable polyhydroxy compds. include inositol ' (II), quebrachitol (III), pinitol and dambonitol. The resins, which are compatible with cellulose dorivs., may be used, if desired with the addn. of cellulose derivs., pigments, fillers, oils and plasticizers, in the manuf, of coating compns. for metal and wood or molding. Among examples, (1) com. III is condensed with phthalic anhydride (IV) alone or in the presence of linseed oil fatty acids with or without tung oil, or a mixt. of tung oil, cyclohexanol and I, and (2) II is heated with linseed oil and the product esterified with IV." From C.A.

Butler, W.H. (to Bakelite Corp.) EMULSIONS CONTAINING / DRYING OIL ESTER RE IN COPOLYFER. U.S. 2,437,293 (Mar. 9, 1948); C.A. <u>42</u>, 4372 (1948) Aqueous emulsions suitable for coatings are produced from esters prepared from the adduct of cyclopentadiene and maleic anhydride, a fat acid (which might be eleostearic) and a polyhydride alcohol with or without a drying oil such as tung oil. The copolymers of such a resin and tung oil polymerize twice as fast as the resin alone and three times as fast as tung oil alone.

Butler, W.H. (to Bakelite Corp.)

COATING COMPOSITION OF FATTY DRYING OILS REACTED WITH FATTY ACID MODIFIED POLYHYDRIC ALCOHOL ESTERS OF CYCLOPENTADIENE MALEIC ADDUCT.

U.S. 2,452,992 (Nov. 2, 1948); C.A. <u>44</u>, 350 (1950)

"An ester resin composed of the cyclopentadiene adduct of maleic anhydride and a fatty acid contg. 5-22 C atoms with a polyhydrio alc. in combination with a drying oil ("such as tung oil"), or semidrying oil, yields a coating compn. Ester resin causes marked acceleration in polymerization on processing when compared to drying oil alone." From C.A.

In one illustration 1 part of an ester resin(solidification time at 250°, 40 min.) was combined with 2 parts of tung oil (solidification time, 275 min. at 250°) to give a product with a solidication time of 11 minutes under the same conditions.

Canadian Industries, Ltd. (Gauerke, C.G.) COATING COMPOSITION CONTAINING BETA-ELEOSTEARIN Can. 305,654 (Nov. 11, 1930); C.A. <u>25</u>, 834 (1931) "A coating compn. contains run β-eleostearin, a modified glyptal resin, high-boiling gasoline and cobalt drier." From C.A.

Canadian Industries, Ltd. (Stauffer, Wm. 0.) CRYSTALLIZING VAPMISH Can. 310,846, (Apr. 28, 1931):* C.A. <u>25</u>, 3184 (1931) "A crystg. varnish contains 19 parts by wt. of a resin made from glycerol, phthalic anhydride and China wood-oil acids, 38 parts of blown China wood oil, 5.5 parts of Co drier soln., 9.5 parts of solvent naphtha and 28 parts of high-boiling gasoline." From C.A.

Canadian Industries, Ltd. (Gauerke, C.G.) SYNTHETIC RESIN Can. 330,337 (Feb. 21, 1933) C.A. 27, 3351 (1933) "A polyhydric alc. is heated with g-eleostearin substantially free from the other components of tung oil, and the remaining free hydroxyl groups of the partially esterified alc. are esterified with a polybasic org. acid and a resin acid or a drying-oil acid." From C.A.

Compagnie Franciase pour L'Exploitation des Procedes Thomson-Houston IMPROV MENT IN SYMTHETIC RESINS. Fr. 37,234 (July 22, 1930) (Addn. to 654,175): C.A. 25, 2582 (1931)

"The production of artificial resins of the alkyel kind combined with drying oils is described. Thus, a mixt. of glycerol and phthalic anhydride is heated progressively to 200°, a mixt. of phthalic anhydride and one or more fatty acids derived from drying oils (china wood oil, linseed oil or Perilla oil) is added and the heating is continued until the foam disappears, then the desired amt, of drying oil is added, e.g., 10-50% of the wt. of the resin. It is preferable to incorporate the drying oil before complete condensation has taken place. Instead of acids from a drying oil, one or more oxidizable unsatd, acids such as oleic acid, stearic acid or linoleic acid may be used. In another example an unsatd, fatty acid, e.g., an acid derived from linseed oil, is heated with glycerol to 200-250°, linseed oil is then added until a clear soln. is obtained. The soln. is mixed with phthalic anhydride and heated further. The compns. of resin and oil are sol, in acetone, AcOBu, BuOH, triacetin, etc., and may be used as a varnish, etc., or incorporated with fillers for making molded objects." From C.A.

Compagnie Franciase Pour L'Exploitation Des Procedes Thomson-Houston. IMPPOVEMENTS IN THE MANUFACTURE OF CERTAIN ENABELS Fr. 37,670 (Oct. 14, 1930); Addn. to 649,384 (C.A. 23, 2841); C.A. 25, 4724-5 (1931).

> "A coating material, particularly for elec. wires, is made by the reaction of a polyalc, a polybasic acid, an acid derived from a drying oil, a drying oil, a resin acid and a non-drying oil. The products are made insol. and infusible by heat. An example of a mixt, for reaction contains phthalic anhydride 125, glycerol 68, fatty acid from linseed oil 110, colophony 35 and castor oil 18 parts. Another example contains phthalic anhydride 191, glycerol 92, fatty acid from linseed oil 70, linseed oil 66, China wood oil 27, castor oil 12 and colophony 95 parts." From C.A.

Compagnie Francaise pour L'Exploitation des Procedes Thomson-Houston Fr. 39,011 (June 1, 1931); C.A. 26, 1811 (1932) "Addn. to 638,275 (C.A. 23, 293). Glycerol is completely mixed with a drying or semi-drying oil, such as linseed oil or China wood oil, after which phthalic anhydride is added and the esterification is completed. The products find applic-

Compagnie Francaise pour L'Exploitation des Procedes Thomson-Houston RESINOUS COMPOSITIONS BASED ON MODIFIED ALKYD RESINS. Fr. 41,896 (Jan. 26, 1933) (Addn. to 726,745); C.A. <u>27</u>, 4701 (1933)

ation in paint and varnish manuf." From C.A.

"Resins are made contg. the usual constituents of alkyd resins and in addn. drying fatty acids such as fatty acids from linseed oil, China wood oil or cotton oil. One example contains glycerol 122, phthalic anhydride 294, ethylene glycol 31, succinic acid 59 and linseed oil fatty acids 72 parts. Other examples are given." From C.A.

Dowson, E.S., Jr. (to General Electric Co.) RESINCUS CONDENSATION PRODUCT AND METHOD OF PREPARATION. U.S. 1,803,174 (Apr. 28, 1931); C.A. 25, 3855 (1931)

"A product suitable for use as a binder or metal coating, etc., comprises the reaction product of an aliphatic polyhydric alc. such as glycerol and a "polybasic" acid such as phthalic anhydride, a fatty acid derived from a drying oil such as eleostearic acid from China wood oil and a small proportion of H₂SO₁." From C.A.

DuPont de Nemours, E.I., & Co.

IMPROV MENTS IN SYMTHETIC RESINS.

Fr. 652,119 (Oct. 22, 1928); C.A. 23, 3589 (1929)

"Synthetic resins are propd, by heating a polyhydric alc., e.g. glycerol and a polybasic acid, e.g. phthalic acid, to 180-265° with a drying cil [such as tung cil] and a natural resin such as Congo resin. The reaction is carried out in a non-reactive atm. such as CO_2 and is continued until the evolution of steam ceases. The resin may be mixed with cellulose esters or drying cils for the production of varnish." From C_0A_0

DuPont de Namours, E.I., & Co.

IN PROVEMENTS IN SYNTHETIC RESINS AND COMPOSITIONS PREPARED THEREFROM.

Erit. 320,041 (Sept. 27, 1929); Paint Varnish Production Mgr. P. 26 (Apr., 1930); C.A. 24, 2624 (1930)

"The production of synthetic resins by heating, say to 180-265°, a mixt, of a polyhydric alc, other than pentaerythrite, a polybasic acid, and a drying oil acid, with or without other acidic bodies, is carried out by treating in an atm. of CO2, N2, H2 or CO. Alcs. specified for the reaction are glycerol, glycols, mannitol, or polyglycerols, acids include phthalic acid or anhydride, succinic, malic, maleic, fumaric, and tertaric acids and drying oil acids as those obtained by hydrolysis of raw or modified linseed, China wood; perilla, soya bean, and fish oils. Abietic acid or natural resins, particulorly those having an acid no. of at least 50, for instance rosin, copal, or run Congo gum, may be added to the reaction mixto, and the proportion of alc- to combined acid constituents is preferably substantially that required for complete esterification. The reaction is preferably continued until the evolution of water vapour has substantially ceased.

Coating-compns. are obtained by mixing the resins produced with solvents, with or without the addn. of pigments, for instance lithopone, driers, drying oils, or cellulose esters or ethers such as cellulose nitrate or acetate. As solvents esters, kctones or aromatic hydrocarbons mixed or not with alcs. or with alcs. and aliphatic hydrocarbons, are referred to." From Paint Varnish Production Mgr. DuPont de Nemours, E.I., & Co.

IMPROVEMENTS IN SYNTHETIC RESIN,

Brit. 341,012 (Jan. 1, 1931); C.A. 25, 4137 (1931)

"A modified alkyelresin prepd. by esterifying a polyhydric alc. with a "polybasic" acid and pure β -eleostearic acid, with or without a resin acid, is used as a component of paints or other coating compns., e.g., a mixt. of glycerol, phthalic anhydride, raw Congo gum and β -eleostearic acid is gradually heated to 180° and subsequently is heated for a short time to 250° and the product dissolved in naphtha. Among the other starting materials mentioned are: glycol, mannitol, pentaerythritol and malic, succinic, camphoric, tartaric and citric acids. Driers such as Co. linoleate may be added. A method of prepg. β -eleostearic acid from China wood oil is described." From C.A.

DuPont de Nemours, E.I., & Co.

IMPROVEMENTS IN AND RELATING TO FLOOR COVEDINGS AND PROCESSES FOR MAKING THE SAME.

Brit. 354,324 (July 31, 1931); C.A. 26, 5440 (1932) "A tough sticky resinous mass is produced by heating a mixt. of glycerol 171, linseed-oil acids 490, china-wood oil acids 164 and phthalic anhydride 248 parts for 2 hrs. at 300° and similar products may be derived from other generally similar mixts. such as those in which ethylene glycol is used instead of glycerol." From C.A.

DuPont de Memours, E.I., & Co,

INPROVEMENTS IN OR RELATING TO SYNTHETIC RESINS AND THEIR APPLICATION

Brit. 359,365 (Oct. 22, 1931); CaA. 26, 4970 (1932) "A drying or semi-drying oil such as linseed oil, soybeen oil, China wood oil or their mixts. is bleached by heating to 260-290° in the absence of an oxidizing gas but preferably in a current of CO₂ or flue gas, then slightly cooled and mixed with a polyhydric alc. such as glycerol or othylene glycol and esterified with phthalic anhydride, succinic acid, fumaric acid, adipic acid, maleic acid or the like to produce a varnish resin compn. which may be mixed with lithopone and ZnO to form a white enamel." From C.A.

DuPont de Nemours, E.I., & Co. IMPROVEMENTS IN OR RELATING TO COATING COMPOSITIONS. British 396,081 (July 28, 1933); C.A. 25, 663 (1934) "A vehicle which promotes leafing of flake pigments, e.g., flake Al, graphite, mica and flake sulfide pigments, consists of an oil-modified polyhydric alc.-polybasic acid resin having an acid value of 15 or less and driers dissolved in mineral spirits or other solvent to give a soln. having a viscosity between A and F on the Gardner-Holdt scales. The flake pigment may be first coated with substances, e.g., stearic acid, that

enhance the leafing properties. The resins may be formed by

condensing in presence of PbO phthalic anhydride, glycerol. (which may be repliced in part by ethylene glycol) and 45-70% of linseed, China wood, perilla or menhaden oils, or acids derived from these oils." From Core.

Durant, W.W. and Scrutchfield, P.H. (to General Electric Co.) REMINOUS COMPOSITION.

U.S. 1,975,569 (Oct. 2, 1934); C.A. 28, 7563 (1934) "A resincus reaction product which is suitable for coating cloth or paper, etc., is formed from reaction of phthalic anhydride, glycerol, succinic acid, ethylene glycol, abietic acid and China-wood oil." From C.A.

Edgar, D.E. (DuPont de Nemours, E.I. & Co.)

RENINOUS COATING COMPOSITIONS,

U.S. 2,121,690 (June 21, 1938); C.A. <u>32</u>, 6486 (1938) "Articles such as those of sended steel are coated with a nonfrosted and unwrinkled film of a baked resincus compound comprising urea-formaldehyde reaction product and substantial amount of polyhydric alc.-polybasic acid resin modified with a substantial quantity of drying oil subject to frosting and wrinkling in the film which normally causes frosting and wrinkling in the films of such resins; the resin contains polyhydric alc. in combined form in excess of from 5 to 30 percent of that required for complete esterification of the acid reactants." From C.A.

By "drying oil subject to frosting" tung oil is generally implied although one example specifies oiticica oil.

Ellis, Carleton (to Ellis-Foster Co.)

RESINGUE PFODUCTS OR COMPOSITIONS INCLUDING LACQUERS, PAINTS, VARNISHES AND OTHER COATING COMPOSITIONS. U.S. 1,958,614 (May 15, 1934); C.A. 28, 4615 (1934) "A glycerol mixed ester of tung or linseed oil acids, phthalic anhydride and rosin is used in lacquers, etc." From C.A.

Gauerke, O.G.

SYNTHETIC RESINS

Can. 330,337 (Feb. 21, 1933*; C.A. <u>27</u>, 3351 (1933)) "A polyhydric alc. is heated with p-eleostearin substantially free from the other components of tung oil, and the remaining free hydroxyl groups of the partially esterified alc. are esterified with a polybasic org. acid and a resin acid or a drying oil acid." From C.A.

Gauerke, C.G. (to DuPont de Nemours, E.I. & Co.) MIXED SYMTHETIC OIL AND PRODUCT DERIVED THEREFROM. U.S. 1,979,260 (Nov. 6, 1934); C.A. 29, 366 (1935) "A polyhydric alc. such as glycerol is heated with a frosting

drying oil such as China wood oil and the partially esterified alc is heated with the fatty acids obtained from a non-frosting oil such as linseed oil; the resulting mixed acid ester is re-alcoholized by heating with a polyhydric alc. and the partially esterified polyhydric alc. is heated with a polybasic acid such as phthalic anhydride until resinification occurs and a product is formed which is suitable for use as a coating material." From C.A.

Holt, S. (to DuPont de Nemours, E.I. & Co.) COLTING COMPOSITIONS

> U.S. 2,059,948 (Nov. 3, 1936); C.A. <u>31</u>, 563-4 (1937). "With a volatile solvent such as xylene, there is used an intimate mixt. of polyhydric alc.-"polybasic acid" resin modified by 35-75% of monobasic acid including linseed oil acids and China-wood oil acids, together with carbon black 0.5-10% of the amount of the resin, and Fe drier 5-20% and a Pb oxide about 1% or more of the amount of the resin but less than would render the resulting film of a muddy appearance (the resin constituting the major proportion of the compn.") From C.A.

Honel, Herbert (to Beck, Koller & Cc.)

ARTIFICIAL MASS AND PROCESS OF MAKING THE SAME,

U.S. 1,870,453 (Aug. 9, 1932); C.A. <u>26</u>, 5777 (1932) "A mono-ester is formed from a relatively low-mol.-wt. "polybasic" carboxylic acid such as phthalic anhydride and a polyhydric aliphatic alc such as glycerol, and a high-mol. wt. "monobasic" carboxylic acid such as China wood oil acid is added, the mixt. is caused to react with a phenol alc. and the mass is esterified by heating." From C.A.

Honel, Herbert (to Beck, Koller & Co.)

ARTIFICIAL MASS AND PROCESS OF MAKING THE SAME. U.S. 1,870,455 (Aug. 9, 1932): C.A. <u>26</u>, 5777 (1932) "Relates to a compn. formed by the reaction of (1) a highmol-wt. monobasic carboxylic acid, (2) a relatively low-mol.wt. polybasic carboxylic acid or anhydride, (3) a polyhydric alc., and (4) a natural glyceride of a high-mol.-wt. monobasic carboxylic acid such as China wood oil." From C.A.

Hopkins, ^H, ^H, (to DuPont de Nemours, E.I. & Co.) COATED PRODUCT. U.S. 1,771,538 (July 29, 1930): C.A. 24, 4647 (1930) "A primer coating is used contg. a mixed ester having as the alc. component a polyhydric alc. such as glycerol and as the acid component a polybasic acid such phthalic acid and acids obtainable by the hydrolysis of a drying oil such as linseed or china wood oil; over the primer coating there is applied a coating of different compn. such as a pyroxylin lacquer." From C.A.

Hopkins, H. H. & Dermott, F.A. (to DuPont de Nemours, E.I., & Co.) SYNTHETIC RESINS U.S. 2,181,893 (Dec. 5, 1939); C.A. <u>34</u>, 2100 (1940) "A process of producing modified polyhydric alc_-polybasic acid resins that are clear and homogeneous and form rapid and hard drying films comprises heating glycerol, phthelic anhydride, linseed oil acids and China wood oil, the China wood oil constituting between 10-60%, of the combined linseed oil acids and China wood oil content." From C.A.

I.G. Ferbonindustrie, A.-G.

IMPROVEMENTS IN THE MANUFACTURE AND PRODUCTION OF LACQUERS, COMPOSITIONS AND THE LIKE.

Brit. 330,895 (June 16, 1930); C.A. 24, 6041 (1930)

"Collulose others such as ethyl collulose, ethyl butyl collulose and benzyl collulose are incorporated with resincus condensation products from "polybasic" carboxylic acids and esters such as the partial esters of glycerol, sorbitol, pentaerythritol or glycols or their hydroxyalkyl others with acids such as abietic, linoleic, ricinoleic, naphthenic, Lauric and china wood oil acids, and used with various solvents, fillers, collulose esters, other resincus products, oils, driers, etc. Various details and examples are given." From CoA.

I.G. Farbenindustrie, A.-G.

PROCESS FOR PRODUCING COLORED VARMISHES.

Fr. 822,744 (Sept. 27, 1937); C.A. 32, 4808 (1938)

"Transparent colorations are produced in varnishes prepd. by using chemically drying binders such as linseed oil, wood oil or the condensation products of polyhydric alcs., or polybasic acids and drying oils, by incorporating in the varnishes org. dyes in soln. in org. solvents contg. 0." From C.A.

Iliff, J.W., and Robinson, Paul (to DuPont de Nemours, E.I. & Co.) ENAMEL-LIKE COATING COMPOSITIONS.

U.S. 1,986,930 (Jan. 8, 1935); C.A. 29, 1668 (1935)

"A drying oil such as linseed and China wood oils and glycerol are heated together, the glyceride thus formed is further heated with phthalic anhydride until resinification occurs, and the resulting resin is blended; without heating, with a heatpolymerized drying oil, suitably in such proportions that the first mentioned drying oil constitutes about 58% of the resin." From C.A.

Imperial Chemical Industries, Ltd. (Morgan, H.H., and Drummond, A.A.) SYNTHETIC RESINS AND VARMISHES.

Brit. 329,335 (Nov. 13, 1928)*; C.A. 24, 5517 (1930)

"A substituted polyhydric alc, such as glyceryl monobenzoate or mono-or di-acetin, and polybasic acid anhydride, such as phthalic anhydride, are condensed in the presence of glycerol esters of fatty acids which do not contain an OH group, such as tung oil or similar drying oil, in the presence or absence of an org. solvent. Driers, pigments, etc. may be added and varnishes or solid products may be obtained." From C.A. Imperial Chemical Industries, Ltd. (Baird, W., Hill, R., and Walker, E.E.) SYNTHETIC RESINS.

Brit. 328,003 (Jan. 9, 1929)*; C.A. 24, 5173 (1930)

"A polyhydric, alc. such as glycerol is condensed with a 'polybasic' acid such as phthalic anhydride in the presence of a monocarboxylic acid such as butyric, stearic or oleic acid, and drying oil such as linseed or China wood oil is incorporated before or during the condensation. Fatty acids from drying oils also may be used, and products are obtained suitable for use with solvents and driers for making rapid drying varnishes or enamels." From C.A.

Imperial Chemical Industries, Ltd.

INPROVEMENTS RELATING TO VARMISHES BASED ON SYNTHETIC RESINS AND TO SYNTHETIC RESINS.

Fr. 683,290 (Feb. 25, 1930); C.A. 24, 4648 (1930)

"The invention is divided into four parts: (a) Synthetic resins are proped, by heating a polyhydric alc, such as glycerol with a dibasic acid anhydride such as phthalic anhydride and a glycerol fatty acid ester such as wood oil under the action of heat with compds. contg. OH groups such as aliphatic alcs., cyclohexanol, ethyl lactate or ethylene glycol. (b) Varnishes are prepd, by incorporating phenolic compds, and CH2O with fatty acid esters in the presence of a volatile org. solvent. (c) A varnish having as a basis a synthetic resin is prepd. by condensing a substituted polyhydric alc. and a polybasic acid in the presence of glyceryl esters of fatty acids such as drying oils and with or without org. solvents. (d) Varnish is propd. by heating raw tung oil with linseed or perilla oil or natural or synthetic resins in the presence of volatile org. solvents; a small quantity of a dehydrating chloride or H2SO4 or KHSO/ is then added. Several modifications and examples in each part with details of the process are given." From C.A.

Imperial Chemical Industries, Ltd.

IPPROVEMENTS RELATING TO THE PREPARATION OF SYNTHETIC RESINOUS COMPOSITIONS.

Fr. 687,894, (May 5, 1930); C.A. 25, 8356 (1931)

"Resins are made by condensing a polyhydric alc. with a polybasic acid in the presence of one or more mono-carboxylic acids, a drying oil being incorporated at any stage. Thus, glycerol, phthalic anhydride and oleic acid are heated to 200-210° and linseed oil is added to form a clear brown resin. The cleic acid may be replaced by linseed oil acids and the linseed oil by China wood oil." From C.A.

with resins such as those formed from glycerol and phthalic anhydride or similar components is facilitated by replacing

438

some or all of the polyhydric alc. by a reaction product of a polyhydric alc. with a lower aliphatic aldehyde such as CH_2O ; e.g., glycerol and polymerized CH_2O are condensed together, then phthalic anhydride and tung oil or kinseed oil, or phthalic anhydride, tung oil, colophony and glycerol are added and the mixt. is heated until a homogeneous resin is produced. Varnishes prepd. from such products dry rapidly in the air or when heated and their drying may be facilitated by adding substances such as Co linoleate." From C_0A_0

Imperial Chemical Industries, Ltd., and Baird, W.

DERIVATIVES OF POLYHYDRIC ALCOHOL-POLYBASIC ACID CONDENSATION PRODUCTS,

Brit. 358,095 (Oct. 5, 1931): C.A. 26, 6165 (1932)

"Condensation products formed from glycerol and phthalic anhydride (with or without castor or tung oils) are reacted with an alkali metal hydroxide or a carbonate, borate or sulfide of an alkali metal, in the presence or absence of monohydric alcs., "monobasic acids" or fatty oils to form a water-sol. product of an acid value not less than 40 which may be used for making films rendered water-insol by treatment with HOAc or HCL. Soveral examples are given." From C.A.

Kienle, R.H. (to General Electric Co.)

RESIMOUS CONDENSATION PRODUCTS AND PROCESS OF MAKING THEM. U.S. 1,893,873 (Jan. 10, 1933); C.A. 27, 2319-20 (1933) "Resinous products are formed from a polyhydric alc., a "poly-basic" aromatic acid such as phthalic anhydride and fatty acids such as those derived from China wood oil." From C.A.

Canadian General Electric Co., Ltd. (Kienlo, R.H., and Schlingman, P.F.)

Can. Pat. 369,326 (Oct. 19, 1937)*; C.A. <u>32</u>, 2248 (1938) "Malcic anhydride is treated with **a** substance contg. the eleostearic acid radical and the product is made to react with a polyhydric alc. Soveral examples are given. The resins are heat-convertible to flexible products, are readily sol. in the A-Stage in warm drying oils, sol. in solvent naphtha, have a marked benzene tolerance, and will not air-dry satisfactorily except when blended with drying cils." From C.A. PHOCESS OF PREPARING OIL ACID MODIFIED ALKYD MATERIAL, U.S. 2,459,176 (Jan. 18, 1949); C.A. 43, 2815 (1949)

"An alkyd which is miscible with fatty oils and sol, in petroleum solvents is prepd, by quickly heating linseed fatty acid monoglyceride (acid no. 10-20) 1436, and (CHCO)₂O 432 g., in an atm. of CO₂. After heating at 450°F., 7-8 min. the mass is dumped into 1800 g. alkali-refined linseed oil and stirred in well. pon cooling to 25°, the product is miscible with other oils and sol, in mineral spirits." From C_0A_0

Monoglycerides of tung oil acids are not suitable for reaction with maleic anhydride by this procedure because the whole mass may gel. When a monoglyceride of some fatty acid has been reacted with maleic anhydride it may be satisfactorily added into tung oil or any other drying oil.

Moore, C.G. (to Glidden Co.)

PEOCESS OF PREPARING OIL-ACID MODIFIED ALKYD MATERIAL. U.S. 2,461,564 (Feb. 15, 1949); C.A. <u>A3</u>, 3216 (1949). "Equimol. proportions of glycerol and fatty acids from drying or semi-drying oils, e.g., linseed oil fatty acid, soybean oil fatty acid, are dispersed in a drying or semidrying oil, e.g., linseed oil, China-wood oil, soybean oil and the mixt, is heated to about 390-450°F., with or without an inert gas, until the reaction between the glycerol and free fatty acid is at least 54% completed. Maleic anhydride is gradually added to the agitated reaction mixt. in equimol. quantity to the glycerol employed and the temp. is then either raised or lowered. The reaction product is useful for clear or pigmented coatings and inks." From C.A.

Pieper, E.J. (to Armstrong Cork Co.)

RESINOUS PRODUCT AND PROCESS OF MAKING SAME.

U.S. 1,847,783 (Mar. 1, 1932); C.A. 26, 2881 (1932) "A synthetic resi n is formed by the combination and condensation of a mixt. contg. an org. polybasic acid or anhydride, such as phthalic anhydride, glycerol, ethylene glycol and diethylene glycol. Fatty acids such as those of linseed or China wood oils also are used." From C.A.

Rust, ⁹,^B, and Canfield, ^W,^B, (one-half to ⁴ontclair Research Corp. and one-half to Ellis-Foster Co.) NODIFIED DRYING OIL-ALXYD RESINS AND PROCESS OF MANING THEM. U.S. 2,530,315 (Nov. 14, 1950) Drying cil-alkyd resins (which may contain tung oil) are modified by reaction with g-unsaturated monohydric alcohol esters of polycarboxylic acids.

Rust, J.B., and Canfield, W.B. (one-half to Montclair Research Corp. and one-half to Ellis-Foster Co.) FSTER MODIFIED DRYING OIL ALKYD RESINS AND PROCESS OF MAKING SAME. U.S. 2,530,316 (Nov. 14, 1950) This patent describes the manufacture of ester-modified drying oil alkyd resins (which may contain tung oil). See U.S. 2,530, 315.

Scheiber, channes

PROCESS FOR THE PROPARATION OF VALUABLE VARMISH RESINS BY CONDENSATION OF AT LEAST TRIFUNCTIONAL POLYALCOHOLS WITH CON-JUGATED UNSATURATED HIGHER FATTY ACIDS AND POLYBASIC ACIDS OR THELE ANHYDRIDES,

Ger. 543,287 (Feb. 18, 1930); C.A. <u>26</u>, 2609 (1932)

"A trihydric or higher polyhydric alc. is esterified with an unsated, higher fatty acid contg. conjugated double bonds, the proportions being such that at least 2 OH groups remain unesterified. The product is further esterified with a polybasic acid or its anhydride in such proportions that at least 1 OH group is still unesterified. The reactions are effected at 200° or above. Thus glycerol may be heated at 200° with 9,11octadecadiene-1-carboxylic acid (prepd. by splitting off H_2O from ricinoleic acid) until the acid no. is zero, and phthalic anhydride then added with continued heating. Other examples are given. The products are sol. in hydrocarbons, and are useful as varnish ingredients." From CoAe [tung oil acids.]

Société Pour L'industrie Chimique A Bale.

ALKYD-MODIFIED FELAPINE-FORMALDEHYDE RESIN.

Swiss 222,709 (Oct. 16, 1942). C.A. 43, 440 (1949).

"No. 222,707. One mol. of glycerol is heated at 220-240° with 0.25 mol. stearic acid until an acid no. of 6 is obtained. One mol. of phthalic anhydride is added and esterification continued to an acid no. of 42. The product is dissolved in 3 mols. of butanol, heated at 100° for 4 hours with 0.33 mol. hexamethylomelamine, and the excess butanol distilled off. Swiss No. 222,708 uses linoleic acid instead of stearic. Swiss No. 222,709 uses tung oil." From CoA.

(b) Tung Oil - Phenolic Resins

Akahiva, T., and Yanagita, M.

PHENOL RESIN MODIFIED WITH DRYING OIL.

Japan 174,656 (July 29, 1947)*; C. A. 44, 2794 (1950); J. Am. Oil Chemists' Soc. 27, 288 (1950).

"A mixture of phenol (50), formaldehyde (40), butanol (17), and HCl (0.5) is heated for 100 minutes at 90°, tung oil (40) is added, and this mixture is heated at 105° until part of the butanol is vaporized. The oil soluble, semisolid resin has good drying properties." From J. Am. Oil Chemists' Soc.

Alexander, George (to General Electric Co.)

RESINOUS COMPOSITIONS AND LAMINATED ARTICLES PRODUCED THEREWITH. U. S. 2,267,390 (Dec. 23, 1941); C. A. 36, 2647 (1942).

"A heat-curable resinous compn. adapted for making a punch-stock varnish is described. It comprises the reaction product of 1 mol. of a mixt. of substituted phenols with more than 1 mol. of CH_2O , the mixture b.200-225°, consisting of paracresol, xylenols and not exceeding substantially 35% m-cresol and being treated with the CH_2O in the presence both of a catalyst comprising $C_2H_4(NH_2)_2$ and NH_3 and of an oil comprising China wood oil, the resulting compn. having a flow point of about 50-70°, and incorporated with the oil-modified resinous reaction product thus obtained, a clear, liquid, compatible product of reaction of 1 mol. o-cresol with more than 1 mol. CH_2O in the presence both of an alk. condensing agent and of an oil comprising China wood oil in an amt. corresponding to about 20-40% the wt. of the dehydrated o-cresol-formaldehyde resin." From C. A.

Alvarado, A. M., and Ubben, R. T. (to Du Pont de Nemours, E. I. & Co.) COATING COMPOSITION.

U. S. 2,110,073 (Mar. 1, 1938); C. A. 32, 3645 (1938).

"Relates to a rapidly drying varnish contg. a drying fatty oil, varnish solvent, and the resin obtained by heating together rosin, glycerol and a formaldehyde-phenol resin that has been hydrogenated in the presence of a hydrogenating catalyst at a temp. of 140-225° and a pressure of 140-2000 lb. per sq. in., the varnish having less tendency to after-yellowing and drying at least twice as fast as the analogous varnish based on the corresponding unhydrogenated formaldehyde-phenol resin." From C. A.

Auxier, R. W., and Weltman, W. C. (to Mestinghouse Electric Corp.) STABILIZING FHENOLIC RESINS.

U. S. 2,383,283 (Aug. 21, 1945); C. A. 40, 1060 (1946).

"Fhenol-aldehyde resins modified with oils as tung or oiticica oil when in the B stage may be stabilized against rapid aging by the incorporation of 0.1-2.0% of a nitrogenous org. compd. selected from the group consisting of pyridine homologs, lecithins, and dicyandiamide." From C. A.

Baekeland, L. H. IMPROVEMENTS IN VARNISHES AND METHOD OF PREPARING SAME. Brit. 6,293 (1912) (Feb. 20, 1913). An improved varnish can be made by dissolving a phenol-formaldehyde type resin in a mixed solvent composed of liquid oxygen-containing aliphatic compound and a volatile hydrocarbon which is not a solvent for the resin. These varnishes may be compounded with tung oil, oleoresinous varnishes, gutta-percha, asphalt, nitrocellulose, etc. In one example a varnish was prepared from resin (200), methanol (10), acetone (80), and benzene (100).

Baekeland, L. H.

A NEW OR IMPROVED VARNISH AND METHOD OF MAKING SAME. Brit. 6,294 (1912) (Feb. 20, 1913).

A varnish is prepared from a phenol-formaldehyde resin and a solvent mixture emposed of an organic liquid with a boiling point below 100° and a second organic liquid, miscible with the first liquid, immiscible with water and boiling, above 100°. Tung oil, olecresinous varnishes, rubber, gutta-percha, asphalt or nitrocellulose may be included. In an example, a varnish is composed of phenolic resin (100), methanol (75), acetone (40), and anyl alcohol (5).

Bakelite Corp.

VARNISH COMPOSITIONS.

Fr. 693,899 (Sept. 8, 1930); Paint and Varnish Production Mgr. p. 24 (Oct., 1931) (abstract); C. A. 25, 1692 (1931).

"Resins of the phenol-aldehyde or of the glyptal type, capable of being hardened, are mixed with an equal wt. of rosin, or other nonhardening resin, and the mixt. is heatd at 200° for 30-60 min. The resulting resin is very sol. in turpentine and oils to give a varnish which drys in 8-10 min. The rosin serves to render the synthetic resin permanently sol. Varnish may be made directly, for example, as follows: cresol 100, 40% HCHO 100, rosin 100, hexamethylenetetramine 1-1.5 and chinawood oil 200 parts are heated together under reflux for 2 hr. The H₂O is then distd. off. Heating is continued at 250° for 1 hr. and 10-20 parts of Pb or Mn tungstate are added. Turpentine may be added." From Paint and Varnish Production Mgr.

Bakelite Corp. (Turkington, V. H.)

IMPROVEMENTS IN OR RELATING TO SYNTHETIC RESINS AND COATING COMPOSITIONS PREPARED THEREFROM.

British 349,522 (May 27, 1931); C. A. 26, 2072 (1932).

"Synthetic resins are made by heating a phenol and a fatty oil such as tung, linseed, perilla or soybean oil with $(CH_2)_6N_2$ at 190-200°, with or without other methylene-contg. substances such as formaldehyde. Prepn. of coating compns. from the products with various solvents, driers, etc. is described." From C. A.

Bakelite Corp. (Turkington, V. H.)

PROTECTIVE COATINGS.

Can. 317,205 (1931)*; C. A. 26, 1460 (1932).

"A coating compn. comprises in soln. the reaction product of phenol, tung oil, formaldehyde and rosin, and cellulose nitrate in admixt. with said product." From C. A.

Bakelite, G.m.b.H.

VARNISHES FROM WOOD OIL AND SYNTHETIC RESINS.

Brit. 355,827 (May 31, 1929)*; C. A. 26, 4487 (1932).

"The process described in Brit. 349,931 (C.A. 26, 2071) is modified by causing wood oil to combine with the hardenable phenol-aldehyde condensation product in the resole stage in the presence of a solvent and at a temp. (suitably about 130-60°) which will effect combination. Varnishes thus formed harden quickly at a moderate temp. Several examples with details of procedure are given." From C. A.

Bakelite, G.m.b.H.

PROCESS FOR COMBINING HARDENABLE PHENOL-ALDEHYDE CONDENSATION PRODUCTS AND AIR-DRYING OILS.

Ger. 533,798 (July 8, 1930); C. A. 26, 862 (1932).

"The resin and oil is heated in the presence of solvent, with I or I-yielding compds. present to accelerate the reaction. Thus, synthetic resin and wood oil are heated with cyclohexanol in the presence of a small quantity of I." From C. A.

Bakelite, Ltd.

IMPROVEMENTS IN OR RELATING TO VARNISH COMPOSITIONS.

Brit. 455,974 (Oct. 30, 1936); C. A. <u>31</u>, 2030 (1937).

"The compns. comprise a fatty oil, e.g., tung, linseed, castor, soybean, an oil-sol. resin, e.g., rosin, ester gum, copal, PhOH-aldehyde resins, fatty acid- or fatty oil-modified alkyd resins, and a neutral ester of a phenol with a polybasic carboxylic acid. The neutral esters are prepd. from PhOH, cresols, higher-alkylated phenols, alkyl and aralkyl esters of hydroxybenzoic acids, benzylphenols, phenylphenols and a- and β -naphthol on the one hand and phthalic, succinic and maleic acids on the other. Among examples, tung oil and a resin prepd. by the reaction of o-phenylphenol with CH₂O are heated with the reaction product of 2 mol. of Me salicylate with 1 mol. of phthalyl chloride; xylene is then added together with a Co or Pb drier." From C. A.

Beckacite Kunstharzfabric G.m.b.H.

PROCESS FOR THE PRODUCTION OF HOMOGENEOUS PRODUCTS FROM DRYING OILS AND THE LIKE AND RESOLS.

Ger. 743,668 (Mar. 25, 1943); C. A. 38, 3058 (1944).

"Resols obtained by condensation of excess CH₂O with phenols having 2 unsubstituted reactive positions and at least I higher hydrocarbon radical in a strongly alk. medium and neutralization of the condensation product are treated." From C. A.

Some of the products were prepared by reacting tung oil with phenolic resins.

Birkbys, Ltd., and Buck, A. J.

POTENTIALLY REACTIVE LIQUID COATING COMPOSITIONS.

Brit. 443,798 (Mar. 6, 1936); C. A. <u>30</u>, 5436 (1936).

"A liquid compn. is prepd. by heating together a phenol, e.g., xylenol, a fatty oil, e.g., tung oil, and a metal, preferably Al. The compn. may be caused to react with a hardening agent, e.g., (CH₂O)n, in soln. in PhMe or xylene in the presence or absence of other resins." From C. A.

Canadian General Electric Co. (Ferguson, C. S.) COATING COMPOSITION.

Can. 342,585 (June 26, 1934)*; C. A. 28, 6002 (1934).

"A liquid coating consists of the product of reaction of substantially pure xylenol 45, paraformaldehyde 10.75, triethanolamine 1.5, and raw tung oil 47.75 parts by wt. and a solvent therefor." From C. A.

Clare, I. C. (to Hercules Powder Co.)

VARNISH COMPOSITION.

U. S. 2,283,353 (May 19, 1942); C. A. 36, 6364 (1942).

"Use is made of a reaction product such as may be formed from methyl abietate, an oil-sol. phenol-aldehyde resin and a drying oil such as China wood oil heated to a max. temp. of about 320-600°F." From C. A.

Coleman, R. E.

VARNISH.

Can. 373,170 (Apr. 19, 1938)*; C. A. 32, 4808 (1938).

"China wood oil is heated with about 2-10% of boric acid, an oilsol. phenolic or alkyd resin is added and the heating is continued until a homogeneous blend is obtained." From C. A.

Courtney, R. P. (to Bakelite Corp.)

PLASTIC COMPOSITION.

U. S. 2,207,997 (July 16, 1940); C. A. 34, 8113 (1940).

"A plastic compn. is prepd. by forming an oil-sol. resin from a substituted phenol such as butyl, amyl or benzyl phenol by reaction with HCHO and then removing water from the resin, heating it with tung oil in the presence of ZnO at a temp. of 230° or higher for about 2 hrs. or longer, dispersing the product in a hydrocarbon thinner such as toluene and kneading the dispersion with a filler including wood flour to form a putty-like mass." From C. A.

Delaware Floor Products Co. (Hills, L. H.)

PAINT.

Can. 289,995 (May 28, 1929)*; Paint Varnish Production Mgr. p. 16-7 (Aug., 1929).

"The method of making a paint which comprises heating China wood oil and a phenol resin condensation product between 550° and 585°F., mixing a drier and an additional quantity of the phenol formaldehyde resin condensation product with the heated mixture of wood oil and condensation product, reheating this mixture until all of the condensation product has been dissolved to provide a varnish, then heating a mixture of refined linseed oil and China wood oil to a temperature of approx. 525°F., maintaining the last-named mixture at approx. 550°F., then reducing the temperature rapidly to approx. 450°F., thoroughly incorporating driers in the last-named mixture, reducing the temperature of said mixture to approx. 350°F., to provide a vehicle and thoroughly mixing the varnish with the vehicle." From Paint Varnish Production Mgr.

Drummond, A. A., and Morgan, H. H. (to Imperial Chemical Industries, Ltd.). PROCESS FOR PRODUCING RESINS.

U. S. 2,079,606 (May 11, 1937); C. A. 31, 4838 (1937).

"A reaction mixt. formed of a phenol such as mixed xylenols, an aldehyde such as HCHO and a polyhydric alc. partially esterified with a fatty oil acid such as a mono-glyceride of tung oil acids is heated in an inert volatile org. solvent, such as MeOH in the presence of NaOH (suitably for several hrs. at 110-120°) until a resinous product. contg. the partially esterified alc. as an indistinguishable part, irremevable as such, is formed." From C. A.

Elbel, Ernst and Seiter, Fritz

PROCESS OF PREPARING RAPIDLY DRYING COATINGS.

U. S. 1,963,973 (June 26, 1934); C. A. 28, 5264 (1934).

"There is applied to a base a layer of a plastic substance such as nitrocellulose in alternation with a layer of the transformation product obtained by reaction of a phenol-aldehyde resin with an air-drying oil such as tung oil and esterifying the resulting product to substantial completion by an org. acid anhydride such as Ac₂O or org. acid chloride. various examples are given." From C. A.

```
Ellis, Carleton (to Ellis-Foster Company)
```

ANTIFOULING COMPOSITION.

U. S. 944,420 (Dec. 28, 1909); C. A. 4,681 (1910).

"A condensation product of equal parts CH₂O (40% soln.) with phenol 2, CuCO₃ 2, CaSO₄ 3, S 0.5, Chinese wood oil 2, a resinous binder, as lime-hardened rosin 4, and a volatile vehicle, as naphtha 4 and benzine 2 parts." From C. A.

Engle, L. S. (to Interchemical Corp.) FINISHING COMPOSITIONS.

U. S. 2,293,428 (Aug. 18, 1942); C. A. 37, 1052 (1943).

"A varnish which is made from China-wood oil and oil-sol, phenolformaldehyde resin, and which otherwise during storage would increase in viscosity markedly and progressively, and eventually gel, is maintained substantially uniform on storage by the addn. of terpinolene." From C. A.

Ferguson, D. S. (to General Electric Co.)

PHENOL-AIDEHYDE-DRYING OIL RESIN COMPOSITION AND PROCESS OF MAKING SAME.
U. S. 1,896,842 (Feb. 7, 1933); C. A. 27, 2831 (1933).
"A liquid coating compn, is prepd. by the reaction together of xylenol, an aldehyde such as paraformaldehyde, triethanolamine and a drying oil such as China wood oil. Solvent naphtha and "mineral spirits" may be added." From C. A.

Gardner, H. A.

IMPROVEMENTS IN PIGMENTS AND FILM-FORMING COMPOSITIONS CONTAINING THE SAME. Brit. 455,762 (Oct. 27, 1936); C. A. <u>21</u>, 2029 (1937). Compositions containing Pb phthalate (I), as a pigment -- "Among examples, (1) a house paint comprises linseed oil, I, turpentine and Pb-Mn drier, and (2) a white quick-drying film-forming compn. is made by grinding I into a varnish made by cooking a PhOH-CH₂O resin with tung oil and adding turpentine and drier." From C. A.

Horn, A. C.

PAINT COMPOSITION AND PROCESS OF MAKING SAME.

U. S. 1,048,536 (Dec. 31, 1912); C. A. 7, 712 (1913).

"Paint containing casein, borax, a neutral salt, PhOH-CH₂O condensation product, tung oil, a pigment, basic Cr sulfate and $H_2^{2}O$." From C. A.

I. G. Farbenindustrie, A.-G.

PROCESS FOR THE PRODUCTION OF RESINOUS CONDENSATION PRODUCTS FROM FATTY ACIDS, POLYHYDRIC ALCOHOLS, PHENOLS AND ALDEHYDES.

Ger. 576,714 (Apr. 29, 1930); C. A. 28, 352 (1934).

"Resinous condensation products are produced by condensing polyhydric alcs. partly esterified with fatty acids, with phenols and treating the product with CH_2O . Alternatively, the polyhydric alc. can be condensed with a phenol, then partly esterified by a fatty acid, and finally treated with CH_2O . In an example, the mono-ester of glycorol and lauric acid is condensed with PhOH in the presence of ZnCl₂, and treated with $(CH_2O)_x$ to give a mass useful in the lacquer industry." From C. A.

Imperial Chemical Industries, Ltd. (Drummond, A. A., and Morgan, H. H.) IMPROVEMENTS IN AND RELATING TO SYNTHETIC RESIN VARNISHES AND SYNTHETIC RESINS.

Brit. 345,310 (Sept. 13, 1929); C. A. 26, 324 (1932).

"Phenol-aldehyde condensation products which may contain 20% or more of fatty acid esters such as those derived from tung or linseed oil, which are sol. in alc., ketone, or ester solvents but insol. in hydrocarbon solvents, are rendered sol. in the latter and substantially insol. in the solvents first mentioned, by heating them to about 110-160°. Several examples are given, the products may be used in making varnishes, with various solvents, driers and coloring substances." From C. A.

Imperial Chemical Industries, Ltd., and Strafford, N.

IMPROVEMENTS IN AND RELATING TO RESINOUS CONDENSATION PRODUCTS. Brit. 350,896 (Feb. 15, 1930); C. A. <u>26</u>, 3125-6 (1932).

"Products suitable for use in varnishes are obtained by condensing a phenol, formaldehyde and tung oil or castor oil or their mixts., with or without adding colophony or natural resins, in a closed vessel, in the absence of a catalyst, and then dehydrating in vacuo." From C. A.

International Printing Ink Corp. (Frishkorn, M. W.)

IMPROVEMENTS IN OR RELATING TO CANS OR LINE METAL FOOD CONTAINERS. Brit. 468,383 (July 2, 1937); C. A. <u>31</u>, 8965 (1937).

"Cans for preserved foods, e.g., particularly those of an alk. character, e.g., asparagus, spinach, are coated internally with a film that includes particles of mica or other inert substance of overlapping plate-like structure. The coating may be applied as a varnish, set by baking and consist of a PhOH-CH₂O resin treated with a softening material, e.g., rosin, a drying oil, e.g., tung oil, and about 10% of mica. The film may contain also a small proportion of ZnO." From C.A.

Kittredge, H. G., and Turner, A. J. (to Kay and Ess Chemical Corp.) ENAMEL AND VARNISH.

U. S. 2,069,252 (Feb. 2, 1937); C.A. 31, 2030 (1938).

"A compn. capable of drying in a hard irregular finish upon being baked at a temp. of about 93-107° comprises a varnish composed of phenolic aldehyde resin 1, colophony 8, glycerol 1 part and raw Chinawood cil, Pb linoleate, Co linoleate and petroleum naphtha; and a second varnish which is composed of a phenolic resin which is a condensate of pure phenol, raw China-wood cil, toluol and a petroleum naphtha; together with addnl. raw China-wood cil, a thinner of toluol and pctroleum naphtha, and a light color paste ground in spar varnish. Various modifications are described." From C. A.

Meier, Egon

PROCESS FOR THE PRODUCTION OF COATING OR PORE-FILLING COMPOSITIONS FOR USE UNDER NITROCELLULOSE LACQUERS.

Ger. 625,399 (Feb. 14, 1926); C. A. <u>30</u>, 3262 (1936).

"Suitable mineral fillers and pigments are mixed with a nitrocellulose lacquer and an oil varnish contg. a phenol-CH₂O-colophony resin and wood oil or linseed oil, which may be thickened. A sp. compn. is described." From C. A.

Meigs, J. V. (to Plastix Corp.) RESINOUS PRODUCT AND PROCESS OF MAKING SAME. U. S. 1,868,216 (July 19, 1932); C. A. <u>26</u>, 5221 (1932). "Relates to a resinous product such as may be obtained by condensing a phenol and dextrose and mixing the product with (CH₂)₆N₄ and China wood oil." From C. A.

Novak, I. J. (to Raybestos-Manhattan, Inc.) LIQUID SATURATING OR COATING MATERIAL AND PROCESS OF MAKING SAME. U. S. 1,952,725 (March 27, 1934); C. A. 28, 3605 (1934). "A fluid cresylic acid aldehyde condensation product contg. 3-5% combined N (which may be derived from NH₃) and which is sol. in fatty oils and capable of transformation by heat to an infusible state is used with China wood oil, the mixt. being transformable by heat into an infusible product." From C. A.

Patentverwertungs-G. m.b.H. "Hermes" VARNISH RESISTANT TO COLD.

Fr. 881,288 (Jan. 22, 1943).
For low temperature applications a varnish is prepared from tung oil
and a reactive phenolic resin.

Reynolds, H.C., Jr. and Kellog, H.B. (to Standard Oil Development Co.) ANTISKIMNING AND WEATHER-RESISTING AGENTS FOR DRYING OIL COMPOSITIONS. U. S. 2,307,158 (Jan. 5, 1943); C. A. <u>37</u>, 3623-4 (1943). "Tri-p-tolyl phosphite about 0.01-0.5% is added, as a neg. oxidation catalyst, to a compn. previously prepd. and contg. ingredients such as tung oil, a phenol resin, and a pos. oxidation catalyst, such as one contg. Mn and Co." From C. A.

Rust, J. B. (to Ellis-Foster Co.)

OIL VARNISH AND PROCESS OF MAKING SAME.

U. S. 2,096,764 (Oct. 26, 1937); C. A. <u>32</u>, 374 (1938).

"In prepg. a light colored varnish, tung oil is used with a resinous product formed by treating crude coal-tar phenols consisting largely of m-cresol or sym. xylenol with acetaldehyde or paraldehyde, and the oil and resin are cooked together at temps. above 200° so that a bleaching action is effected and a product obtained which is transparent in thin films." From C. A.

Rust, J. B. (to Ellis-Foster Co.)

ALKALI-RESISTING PHENOLIC-ALDEHYDE SICCATIVE COMPOSITION AND PROCESS OF MAKING SAME.

U. S. 2,142,077 (Dec. 27, 1938); C. A. 33, 2745 (1939).

"A coating compn. is made by cooking tung oil and another drying oil such as linseed oil with a normally oil-sol. phenolic-aldehyde resin in the usual varnish-kettle practice except that a small amount of oxalic acid is included in the mixt. of oil and resin during the heat bodying operation, the temps. employed being substantially below 200° except for a final, brief heating at about 270° to eliminate oxalic acid by volatilization." From C. A.

Seebach, Fritz

PROCESS FOR THE FRODUCTION OF COMBINATION PRODUCTS FROM RESOLS AND WOOD OIL.

Ger. 733,639 (Öct. 26, 1938); C. A. <u>38</u>, 1052-3 (1944).

"Resol and wood oil are combined by heating the two in a suitable solvent. Prior to this step the NH,OH used in the prepn. of the resol as catalyst and still remaining in the resol is neutralized by treating the resol with an acid or a substance that forms an acid." From C. A.

Seebach, Fritz (to Bakelite Corp.)

LACQUER AND ITS PREPARATION.

U. S. 2,167,127 (July 25, 1939); C. A. <u>33</u>, 9022 (1939).

"An aq. dispersion of a phenol-aldehyde resin and wood oil suitable for use as a lacquer is made by heating about equal parts of the resin and wood oil together with a wood-oil acid in the presence of cyclohexanol, distg. off at least part of the cyclohexanol, and passing the product, in the form of a heated liquid, into water made alk." From C. A.

Turkington, V. H. (to Bakelite Corp.)

VARNISH COMPOSITIONS.

U. S. 2,075,839 (Apr. 6, 1937); C. A. <u>31</u>, 3718 (1937).

"A drying oil such as tung oil is heated (suitably to about 280°) with an oil-sol. synthetic resin (such as one formed from o-phenylphenol and CH₂O) and a neutral phenol ester of a dibasic carboxylic acid such as a neutral phenol ester of phthalic acid." From C. A. Turkington, V. H., and Butler, W. A. (to Bakelite Corp.)

DRYING OIL COMPOSITION.

U. S. 1,988,615 (Jan. 22, 1935); C. A. 29, 1667 (1935).

"A liquid compn. suitable for coating surfaces exposed to the weather is prepd. by heating an oil-sol. phenol-adlehyde reaction product having an accelerating effect upon the drying of the oil with a substantially equal wt. of China wood oil until a sample remains clear on cooling, adding drying oil such as linseed oil to the mixt. in, e.g. about 8 times the original quantity of oil. and heating the mixt. at about 200° or higher to obtain the desired viscosity." From C. A.

(c) Copolymers

Arvin, J. A., and Gitchel, W. B. (to Sherwin-Williams Co.) RESINOUS ESTERS OF POLYHYDRIC ALCOHOLS WITH POLYMERS OF STYRENE AND RESIN ACIDS AND METHOD OF PREPARATION THEREOF.

U. S. 2,457,769 (Dec. 28, 1948); C. A. <u>43</u>, 2448 (1949).

"A resin acid contg. a free carboxylic acid group (e.g. rosin) is polymerized with styrene at above 300°F. and at atm. pressure, and the resultant polymer is esterified with glycerol, penterythritol, polypentaerythritol, or sorbitol at temp. around 400° to 750°F., with or without the catalyst CaO. The resultant ester is bodied directly with the drying oil [e.g.tung] producing varnishes and enamels." C. A.

Berger, L., & Sons, Ltd. (Wakeford, L. E., Hewitt, D. H., and Davidson, R. R.) MANUFACTURE OF INTERPOLYMERS OF STYRENE WITH FROSTING DRYING OILS AND OF COATING COMPOSITIONS OBTAINED THEREFROM.

> . Brit. 580,913 (Nov. 3, 1944)*; Brit. Chem. Abstracts 1947, B, II, 63. "A non-frosting, sol., compatible styrene-oil polymer is prepared by heating styrene and an unpolymerized frosting drying oil (e.g. tung or oiticica oil) in a solvent comprising a monocyclic a-terpene (e.g. dipentene), with or without an aromatic and/or aliphatic hydrocarbon (e.g. xylol or mineral spirits). The styrene and terpene are added in determined portions during the reaction." From Brit. Chem. Abstructs.

Bobalek, E. G. (to Arco Co.)

INTERPOLYMER PRODUCED FROM POLYHYDRIC ALCOHOL, POLYBASIC ACID, AND INTERPOLYMER OF MONOVINYL ARGMATIC COMPOUND, OLEFINIC ACID, AND DRYING OIL OR OIL FATTY ACID.

U. S. 2,470,752 (May 24, 1949); C. A. <u>43</u>, 6433 (1949).

"A superior resin base for surface coatings is made from an ungelled resinous interpolymer produced from the reaction of (a) a monovinyl aromatic compd., such as styrene, a-methylstyrene, flurostyrene, or similar compd. in amt. of 10-60% by wt. with (b) a monocarboxylic olefinic ocid contg. a single olefinic C-C linkage and the carboxyl group as sole functional group in amt. of 2-25% by wt. of the monovinyl aromatic compd., such as methacrylic, acrylic, or cinnamic acid, and with (c) a drying oil fatty acid having av. double bond content and Woburn iodine no. between 133-274, such as dehydrated castor oil,

conjugated soybean oil, etc. The rest, 70-20% by wt., contains a polyhydric alc. with at least 3 and no more than 6 OH groups per mol. and a polybasic org. acid selected from a group consisting of satd. and unsatd. polybasic acids contg. carboxyl groups as sole functional groups, such as malonic, phthalic, adipic, or others. The first 3 items are caused to react together in presence of a peroxide catelyst to a predetd. n, the polybasic acid and polyhydric alc. are added either separately or admixed, and the polymerization process is continued. The resultant resin yields very high flexibility and resistance to water or alkali." From C. A.

The unsaturated drying oil or acid should have an average double bond content (iodine no.) as high as that of dehydrated castor oil (133 Woburn) but no higher than that of β -eleostearic acid (274 Woburn). Acids are easier to use than oils for the tendency toward gelation is less.

Dow Chemical Co.

IMPROVED FRODUCTION OF SYNTHETIC RESINS.

Brit. 536,590 (May 20, 1941); C. A. 36, 1696 (1942).

"The resins are obtained by heating a mixt. consisting essentially of a polymerizable vinyl aromatic compd. and between 0.1 and 2.0% of tung oil or oiticica oil, at a temp. ranging from 30° to 250°, in absence of a solvent or emulsifying medium for the vinyl aromatic compd." From C. A.

DuPont de Nemeurs, E.I., & Co. (Lawson, N. E., and Sandborn, L. T.) IMPROVEMENTS IN OR RELATING TO THE POLYMERIZATION OF VINYL DERIVATIVES AND IN COATING COMPOSITIONS.

Brit. 392,924 (May 15, 1933); C. A. 28, 352 (1934).

"Vinyl compds., e.g., vinyl acetate, chloride or styrenc, are polymerized in the presence of non-polymerized, nonoxidized drying oils in the absence of H_2O . Among examples (1) vinyl chloride and raw linseed oil are polymerized in the presence of Bz peroxide, (2) styrene and alkali-refined linseed oil are polymerized in soln. in ethylbenzene and (3) a spraying enamel consists of the resin of example (2), dixylylethane, a drier and "Titanox" pigment dissolved in a mixt. of C_6H_6 , PhMe and xylene." Cf. C. A. 27, 3837. From C.A.

Example 3 states "A mixture of 1500 g. vinyl chloride, 150 g. raw chine wood oil, 1000 g. toluene, and 45 g. benzoyl peroxide was passed through a 3-foot, lead-lined tube having a capacity of 463 cc at a rate of 300 cc per hr. under a pressure of 500 lbs./sq. in. and at a temperature of 115-120°C. The solution obtained in this way contained 20% solids and had a viscosity of about 0.1 poise at 20°C. Clear films were obtained from this solution."

DuPont de Nemours, E.I., & Co.

IMPROVEMENT IN OR RELATING TO THE PRODUCTION OF INTERPOLYMERS OF HEAT-BLENDED OIL VARNISHES AND POLYMERIZABLE ESTERS. Brit. 548,212 (Sept. 30, 1942); C. A. <u>38</u>, 501-2 (1944).

"The interpolymers are produced by heating together a preformed varnish, obtained by heat-blending a frosting drying oil [e.g. China wood oil] with a small proportion of a varnish gum or rosin, with a polymerizable ester of an a-methylene open-chain aliphatic monocarboxylic scid." From C. A. Du Pont de Nemours, E. I., & Co.

INTERPOLYMERS OF VINYL ESTERS.

Brit. 556,113 (Sept. 21, 1943); C. A. 39, 1325 (1945).

"A monomeric vinyl ester of a monocarboxylic acid is interpolymerized by heating with a reaction product of a frosting drying oil [e.g., china wood oil] with a minor proportion of an a, β -unsatd. acid having an ethylenic double bond between the C next to the carboxyl group and the C once removed from it or a simple deriv. of the acid, such as an ester, anhydride, amide or nitrile. The interpolymers are useful in the prepn. of coating compns." From C. A.

Ellis, Carleton (to Ellis-Foster Co.)

REACTION PRODUCT AND PROCESS OF MAKING SAME.

U. S. 2,033,131 (Mar. 10, 1936); C. A. 30, 3261 (1936).

"A reaction product of tung oil with an acidic compd. contg. the radical -CC-C=C- such as maleic acid (suitably prepd. by heating up to 282°) is used with various other ingredients. Numerous examples are given." From C. A.

Ellis, Carleton (to Ellis-Foster Co.)

SICCATIVE COMPOSITION AND PROCESS OF MAKING SAME.

U. S. 2,063,369 (Dec. 8, 1936); C. A. <u>31</u>, 892-3 (1937).

"An ammonia-sol. comprises an unsatd. org. acid reaction product with tung oil such as the reaction product of tung oil with maleic acid and the reaction product of rosin with an unsatd. org. acid such as maleic acid. Numerous examples are given." From C. A.

Flint, R. B., and Rothrock, H. S. (to Du Pont de Nemours, E.I., & Co.) COPOLYMERS OF STYREME WITH FROSTING DRYING OIL VARNISHES. U. S. 2,225,534 (Dec. 17, 1940); C. A. <u>35</u>, 2349 (1941). "Interpolymers suitable for use in coating compns. are formed of

styrene with a performed, heat-blended resin-frosting drying-oil varnish (suitably formed with China-wood oil), the products being adapted for coating various materials." From C. A.

Flint, R.B., and Rothrock, H.S. (to Du Pont de Nemours, E.I., & Co.) COPOLYMERS OF ESTERS OF ALPHA-MATHYLENE OPEN-CHAIN ALIPHATIC MONOCARBOXYLIG ACIDS WITH FROSTING DRYING-OIL VARNISHES. U. S. 2,276,176 (Mar. 10, 1942); C. A. <u>30</u>, 4726 (1942).

"An interpolymer of a preformed heat-blended frosting drying-oilvarnish gum varnish with a polymerizable ester of an a-methylene openchain aliphatic monocarboxylic acid such as methyl methacrylate is prepd. which is of reduced frosting character." From C. A. The drying oil used in most of the examples and in 12 of the 20 claims is china wood oil.

Foster, N. C. (to Westinghouse Electric Corp.)

RESINOUS COMPOSITIONS AND USE THEREOF IN FORMING ELECTRICAL MEMBERS AND LAMINATED PRODUCTS.

U. S. 2,482,086 (Sept. 20, 1949); C. A. 44, 872 (1950).

"A thermosetting resin was prepd. which cured without evolution of water or gases. Linseed oil 80, castor oil 20, and maleic anhydride 30 parts were heated with stirring to 175-190° for 8-12 hrs. The reaction product 75 was mixed with styrene 25 parts, 0.5% benzoyl peroxide added, and the mixt. heated in a mold at 125° for 1 hr. A flexible molding was obtained. Other oils [such as tung oil] may be used. These resins are useful as potting compds. for elec. applications." From C. A.

Gerhart, H. L., and Adams, L. M. (to Pittsburgh Plate Glass Co.) SYNTHETIC GUM FOR PAINTS AND VARNISHES.

U. S. 2,390,530 (Dec. 11, 1945); C. A. 40, 1048 (1946).

"A synthetic gum is prepd. by copolymerizing a polymer of cyclopentadiene contg. 2-5 cyclopentadiene units with a drying oil such as linseed oil. The cyclopentadiene polymer usually consts of 60-90% of the reaction mixt. The copolymerization may be carried out (a) in the presence of a catalyst such as BF₃ beginning at room temperature and gradually increasing the temp. until a solid polymer results, or (b) by subjecting the oil-cyclopentadiene mixt. to a temp. of 180-260° in an autoclave for 2-4 hrs. The cyclopentadiene polymer generally used is the dimer. Other oils such as soybean, perilla, oiticica, tung, cotton, palm, or sunflower oil may also be used. The synthetic gums into varnishes with linseed oil, etc., by known procedures so that the varnish, exclusive of solvents, contains 40-70% oil. Driers and (or) pigment may be added. The varnishes produced have superior water resistance and dry rapidly to a tack-free state." From C. A.

Gerhart, H. L., and Adams, L. M. (to Pittsburgh Plate Glass Co.) PURIFXING DICXCLOPENTADIENE.

U. S. 2,397,601 (Apr. 2, 1946); C. A. 40, 3938 (1946).

"When a fraction of drip oil contg. dicyclopentadiene is heated to 200° to 300°, cyclopentadiene polymers, (I), of low mol. wt. are formed which are insol. in the normal diluting impurities. A mixt. b₆₀ 78-95° is heated in an autoclave at 200° for 2 hrs. then at 230° for 2 hrs. On cooling, the mass solidifies to a soft slush. The solid polymer can be sepd. from the solvent by: (a) filtration; (b) diln. with acetone followed by filtration; (c) distn. in vacuo to remove nonsolids. I can be copolymerized with unsatd. glycerides, such as linseed oil, [tung oil], or soybean oil, to give either resins or drying oils." From C. A.

Griess, G. A., and Teot, A. B. (to Dow Chemical Co.)

INTERPOLYMERS OF DRYING CILS, MONOALKENYL-AROMATIC HYDROCARBONS AND DIVINYLBENZENE.

U. S. 2,468,747 (May 3, 1949); C. A. 43, 5608 (1949).

"Products are made by the procedures disclosed in U. S. 2,468,748 (following abstr.) except that, as part of the reaction mixt. ethylvinylbenzene and divinylbenzene are added further to control the reaction and to improve the tack resistance at elevated temps. A mixt. of dehydrated castor oil 53, styrene 31.1, a-methylstyrene 13.3 ethylvinylbenzene 0.3%, divinylbenzene 0.2 and Bz₂O₂ 2% is first treated et 150° for 2.5 hrs. and then at 200° for 21.5 hrs. The product, a clear resin, is sol. in alkali-refined linseed oil and PhCH₂. A varnish having 60% solids content is made by dissolving the resin in an equal mixt. of PhCH₃ and mineral spirits. After application of the varnish to a metal panel and curing at 110°, it is found that the film is tack-free after 20 min. and satisfactorily hardened after 4 hours. Adhesion to the metal is good." From C. A.

An average of less than 35, and preferably not more than 25, per cent of the elefinic linkages in the molecules of the drying oil should be conjugated with respect to one another. Employment of a drying oil, e.g. tung oil alone or oiticica oil alone, having a higher degree of conjugation usually results in formation of a nonuniform polymeric product which is not readily or completely compatible with usual varnish or lacquer solvents such as those mentioned above. However, mixtures of conjugated and unconjugated drying oils, e.g. of tung oil and linseed oil, may be used, provided the average degree of conjugation between olefinic linkages is within the limits given above.

Griess, G. A., and Teot, A. S. (to Dow Chemical Co.) DRYING OIL-STYRENE INTERPOLYMERS.

 $\mathbf{H} = 2 / 68 7/2 (\mathbf{M}_{22} - 2 - 10/2) = 0 / 2 - 560$

U. S. 2,468,748 (May 3, 1949); C. A. 43, 5608 (1949). "Products which are useful as varnish resins are made by treating (in the absence of scl.) drying oils [tung] with styrene in the presence of a-methylstyrene and Bz₂O₂. The process gives clear resins which are sol. in the common varnish solvents. The a-methylstyrene aids in preventing "runaway" polymerizations and the Bz202 increases the rate of the controlled reaction. Although a variety of drying oils may be used, it is necessary, in order to obtain clear, sol. products, to use those whose conjugation is below 35%, i.e. linseed, soybean or dehydrated castor oil. To prep. a typical resin, dehydrated castor oil 48, styrene 35, a-methylstyrene 15, and Bz 0, 2 parts by wt. are heated at 150° for 50 hrs., resulting in a clear, yellowish resin contg. 2% volatile unpolymerized material and having a Gardner-Holdt viscosity of Z-6. A varnish can be made by dissolving 1 part by wt. of the resin in 1 part of an equal mixt. of mineral spirits and xylene, adding Co 0.02, Mn 0.005, and Pb (naphthenates) as driers 0.15 and guiacol 0.1% as an antiskinning agent. Films made from the varnish exhibit good metal adhesion, H20 resistance, pale color, good color retention and excellent durability." From C. A.

Haroldson, Arthur (to Continental-Diamond Fibre Co.)

RESINOUS PRODUCT AND METHOD OF MAKING THE SAME.

U. S. 2,185,080 (Dec. 26, 1939); C. A. <u>34</u>, 2963 (1940).

"A product convertible by heat into an infusible, insol. state comprises the reaction product of an oil-incompatible, heat-convertible, phenol-formaldehyde resin with a reaction product of a double bond of tung oil and a double bond of unsatd. aliphatic, dicarboxylic acid having a

-CO--C=C- group, such as maleic acid, there being present at the time of the conversion of the oil-incompatible resin into the tung oil-phenol-formaldehyde resin only the oil-incompatible resin and the tung oil-dicarboxylic acid reaction product as substantial reactants, the tung oil-phenol-formaldehyde resin yielding no sepn. of the oil during curing of the resin." From C. A.

Huff, C. E. and Clynch, J. H. (to U. S. Rubber Co.) DRYING OIL-NEOPRENE RESINS.

U. S. 2,442,085 (May 25, 1948); C. A. 42, 5717 (1948).

"Improvements in thermal copolymer resins, for use as plasticizers and varnishes, are described. Copolymers of vegetable drying oils having an I no. of at least 100, and 2-chloro-1,3-butadiene (neoprene) are prepd. The ratio of neoprene to oil may be 5 to 20 parts by wt. for every 100 parts by wt. of oil. By heating above 400°F. a viscous, resinous mass, having a viscosity of above 90 centipoises (450°F.) is obtained. Such a mass is claimed to be superior as a footwear varnish." Instead of linseed oil, other common drying oils such as cottonseed, dehydrated castor oil, sardine, tung oil, perilla, menhaden, etc., may

I. G. Farbonindustrie, A.-G. (Bernhard, Hans)

PROCESS FOR THE PRODUCTION OF HIGH GLOSS OIL LACQUERS WHICH SPREAD WELL. Ger. 588,843 (Sept. 3, 1927); C. A. 28, 2204 (1934).

"A lacquer of high gloss is produced by adding aliphatic carboxylic acids with α , β - or β , γ -double bonds to the usual constituents. Thus, a lacquer consists of thick cil made from linseed oil and wood oil. Sorbic acid is added at 100-30°. ZnO is added and subsequently, sangajol, turpentine oil and Co siccative. Other examples are given." From C. A.

I. G. Farbenindustrie, A.-G.

be used.

PROCESS FOR THE PRODUCTION OF CONDENSATION PRODUCTS.

Ger. 686,092 (Mar. 10, 1931); C. A. 34, 6733 (1940).

"Wood oil or the eleostearic acid contained in this or its derivatives are condensed by heating to temps. above 110° with aliphatic a, $\beta \rightarrow$ unsaturated polycarbonyl compds. or with compds. which are converted over into such substances under the reaction conditions, and the condensation product is esterified, interesterified or neutralized if necessary." From C. A.

I. G. Ferbenindustrie, A.-G.

PROCESS FOR THE PREPARATION OF CONDENSATION PRODUCTS.

Fr. 747,416 (Mar. 28, 1933); C. A. 27, 4890 (1933).

"Wood oil or oleostearic acid contained therein or derivs. of this acid are condensed by heating to above 110° with aliphatic polycarboxylic compds. unsatd. in the a, β -position or with compds. giving rise to such compds. under the conditions of working, and esterifying or neutralizing the products obtained. Examples are given of products obtained from wood oil, the acids therefrom and maleic anhydride, maleic acid, citric acid and fumaric acid. The products may be used in making varnishes and artificial compns. and as auxiliary agents in the textile industry." From C. A.

Jordan, Otto, Kolleck, Leo, and Ufer, Hanns (to I. G. Farbenindustrie, A.-G.) BASE FOR COATING COMPOSITIONS.

U. S. 2,054,019 (Sept. 8, 1936); C. A. 30, 7884 (1936).

"As a base for coating compns., there is used an interpolymerized product from a conversion product of a drying vegetable oil such as linseed or China wood oil and a polymerizable vinyl compd. selected from the acyclic and homocyclic ethers and alkyl ketones, contg. at least one vinyl group, such as vinyl ethyl or butyl ether." From C.A.

Koenig, W. J. (to Sloan-Blabon Corp.)

COMPOSITION OF MATTER AND METHOD OF MAKING THE SAME.

U. S. 2,058,597 (Oct. 27, 1936); C. A. <u>31</u>, 280 (1937). "Relates to a condensation of a drying oil to be hardened with an oxyheterocyclic compd. such as coumarone or phthalic anhydride (suitably at a temp. of about 43-60°)." From C. A.

Koenig, W. J. (to Sloan-Blabon Corp.)

COMPOSITION OF MATTER AND METHOD OF MAKING THE SAME.

U.S. 2,058,598 (Oct. 27, 1936); C. A. 31, 280 (1937).

A drying oil such as blown China wood oil used for coating or plastics is hardened by reaction with an oxy-cyclic terpene such as terpineol or fenchone.

Koenig, W. J. (to Sloane-Blabon Corp.)

COMPOSITION OF MATTER AND METHOD OF MAKING THE SAME.

U. S. 2,116,072 (May 3, 1938); C. A. 32, 5238 (1938).

"Hardening of materials such as drying oils for use in varnishes, etc., is effected by condensing a mixt. in which the condensation reactants consist of oxidized drying oil such as that derived from China wood oil having double bonds in conjugate arrangement and an unsatd. hydrocarbon terpene such as dipentene or terpenine at superatm. temp." From C. A.

Koenig, W. J. (to Sloan-Blabon Corp.)

COMPOSITION OF MATTER AND METHOD OF MAKING THE SAME.

U. S. 2,116,073 (May 3, 1938); C. A. 32, 5238 (1938).

"Relates to the hardening of mixts. of drying oil such as blown China wood oil and a cyclic org. compd. contg. the group -C=C-C=O." From C. A.

Lawson, W. E., and Sandborn, L. T. (DuPont de Nemours, E.I., & Co.) POLYMERIZATION OF VINYL COMPOUNDS IN THE PRESENCE OF FILM FORMING MATERIALS.

U. S. 1,975,959 (Oct. 9, 1934); C. A. 28, 7562-3 (1934).

"A vinyl ester or styrene is polymerized in a mutual inert solvent such as ethyl benzene, in the presence of a film-forming material such as cellulose nitrate, a resin such as rosin or ester gum and a drying oil such as China-wood oil, etc. Numerous examples are given." From C. A.

Lycan, W. H., and Gerhart, H. L. (Pittsburgh Plate Glass Co.) COPOLYMERIZATION PROCESS.

U. S. 2,443,044 (June 8, 1948); C. A. 42, 6165 (1948).

"Drying resins having improved color and free from insol. polymeric substances of higher mol. wt. are prepd. by copolymerizing unsatd. glyceride oils with cyclopentadiene or its lower polymers. The cyclic diene is introduced to the preheated oil at a rate to maintain an optimum reaction temp. of between 260 and 315°." From C. A.

Linseed, soya bean, sardine, menhaden, whale, sunflower, tung, and other oils of like nature can be employed.

Mighton, C. J. (to Du Pont de Nemours, E. I., & Co.) INTERPOLYMERS.
 U. S. 2,346,858 (Apr. 18, 1944); C. A. <u>38</u>, 6014 (1944). "Tung oil or other frosting drying oil is heated with methyl methacrylate or other α-β-unsatd. carboxylic acid or ester in the presence of a catalytic amt. of Bz₂O₂, and the product is interpolymerized with monomeric vinyl acetate or other vinyl ester of a satd. carboxylic acid. The polymers dry rapidly to hard, tough, glossy and adherent films free from frost, and are suitable for coating wood, metal, stone, glass, etc." From C. A.
Monsento Chemical Co. SOFT SYNTHETIC RUBBERLIKE MASSES.
SOFT SIMILATIC ROBBERLIAE MASSES. Brit. 572,279 (Oct. 1, 1945); C. A. 42, 789 (1948). "A plastic material is prepd. by polymerizing a mixt. of a 1,3- butadiene hydrocarbon or its halogen deriv. or of isoprene and a vinyl cyanide in an emulsion contg. a stabilizing agent and a catalyst in the presence of a minor proportion of a drying oil, such as tung oil." From C. A.
Morrell, R. S., Marks, Sydney, and Samuels, Henry
LACQUER VARNISHES. Brit. 407,957 (Mar. 19, 1934); C. A. 23, 5691 (1934). "Resinous compds. cre prepd. by heating β -eleosteeric acid (I) with (a substance capable of yielding) maleic anhydride (II) and subsequently esterifying the product, or by heating β -eleosteerin (III) with II. I or II may be obtained from tung oil by treating with I, S or S chlo- ride, or by the action of light. β -Couepin, derived from oiticica oil, may be used instead of III. Among examples (1) III is heated with II in a current of N to give a viscous mass sol. in Me ₂ CO, alc., Et ₂ O, C ₆ H ₆ , turpentine and glacial AcOH and miscible with II inseed oil, the solns. of the product, with or without added driers, drying to a hard film, (2) the product obtained by treating a mixt. of tung oil and linseed oil with I is dissolved in turpentine, treated with II and a Co lincleate drier is added to yield, with or without an added resin ester, a resinous phenol-aldehyde, condensation product or di- or poly- hydric alc., a varnish, and (3) the product of the interaction of II and III is dissolved in a mixt. of xylene and BuOH or turpentine together with Co and Mn lincleates and Zn white." From C. A.
Resinous Products & Chemical Co. COREACTION PRODUCTS FROM DRYING OILS AND COPOLYMERS OF CYCLOPENTADIENE
AND STYRENE. Brit. 614,532 (Dec. 16, 1948); C. A. 43, 4029 (1949).
Brit. 614,532 (Dec. 16, 1948); C. R. 42, 462) (1949). "Although drying oils do not react with cyclopentadiene polymers, reaction is accomplished when cyclopentadiene-styrene copolymers are used. The products are useful as film formers." From C. A. Tung oil is one of the group of oils which may be used. Details of the polymerization procedure are given.

Resinous Products & Chemical Co.

COPOLYMERS OF CYCLOPENTADIENE AND STYRENE.

Brit. 614,533 (Dec. 16, 1948); C. A. 43, 4029 (1949).

"This disclosure describes production of cyclopentadiene-styrene copolymers which have excellent aging characteristics, and which can be caused to react with drying oils (e.g. tung oil) as in Brit. 614,532." From C. A.

Rust, J. B. (to Montclair Research Corp.)

MODIFIED DRYING OILS AND FROCESS OF MAKING SAME.

U. S. 2,467,912 (Apr. 19, 1949); C. A. 43, 4873 (1949).

"The bodying and drying properties are improved by heating a drying oil with 1-5% by wt. of an ester consisting of an alc. ester of an olefinic a, β -dicarboxylic ucid, such as diallyl maleate, diallyl fumarate, and bis (2-methylallyl)." From C. A.

Oils that may be used include Ching-wood oil, oiticice oil, linseed oil, soyabean oil, perilla oil, sunflower oil and the like.

Stoesser, S. M., and Gabel, A. R. (to Dow Chemical Go.)

STYRENE-TUNG OIL COPOLYMER.

U. S. 2,190,906 (Feb. 20, 1940); C. A. 34, 4187 (1940).

"A product substantially insol. in common org. solvents and having a high impact strength, suitable for molding, is obtained by polymerizing a mixt. of styrene with about 0.1-2.0% of tung oil (suitably by heating at 125° for 3 days)." From C. A.

(d) Wrinkle Finishes

Agnew, A. M. (to Chadeloid Chemical Co.)

COATED FABRIC AND METHOD OF MAKING SAME.

U. S. 1,980,309 (Nov. 13, 1934); C. A. 29, 366-7 (1935).

"A base material such as a filled fabric is provided with a coating having a crinkled surface obtained without embossing and formed from heat-treated China wood oil, a semi-drying oil such as soy-bean oil or fish oil, and a filler such as Pb₃O₄, PbO, etc." From C. A.

Baronsfeld, Lother

PROCESS FOR THE PRODUCTION OF WRINKLE COATINGS WITH VARNISHES CONTAINING WOOD OIL.

Ger. 508,556 (May 9, 1928); C. A. 25, 834 (1931).

"A wrinkled effect is produced by spraying a solvent liquid over a smooth-dried wood-oil lac. Thus, a smooth-dried coating of a lac contg. collodion, wood oil, Cu resinate, AcOBu and toluene is sprayed with a mixt. of AcOBu, AcOEt and toluene." From C. A.

Bede, J. A.

METHOD OF FINISHING ARTICLES.

U. S. 2,268,012 (Dec. 30, 1941); C. A. 36, 2745 (1942).

"A method of treatment is employed which involves: (a) dipping the article in a low-viscosity coating compn. contg. wrinkle-drying oil, resin and solvent, wherein the solvent is added in excess to provide a liquid coating compn. which will rapidly drain from the article and remove foreign matter, (b) applying thereover a spray coating of a relatively high-viscosity wrinkle-drying compn. while the initial coating is still tacky, this wrinkle-drying compn. comprising wrinkledrying oil, resin and solvent, and (c) baking the coated article to produce a wrinkle finish (the finish coating being applied while heated to about 150-165° F.)." From C. A.

One of the two examples specifies China-wood oil and the other contains blown wood oil.

Beynon, N. T. (to New Wrinkle, Inc.)

FLEXIBLE MATERIAL WITH WRINKLE-TEXTURED COATING.

U. S. 2,456,671 (Dec. 21, 1948); C. A. 43, 2790 (1949).

"Coating compns. designed to wrinkle on the surface have been made from oils contg. conjugated double bonds in their chem. structure and are formulated into varnishes with resins, or incorporated into alkyd resins. A new method of manufg. wrinkling coatings is claimed using these oils and synthetic-rubber latexes, such as butadiene-styrene or butadiene-acrylonitrile copolymers, neoprene latex or polyvinyl chloride latex. Low-temp. baking produces varied shapes and sizes of surface wrinkle in the film depending on the amount and type of oil and latex." From C. A.

"The oils used may be native oils such as tung oil and oiticica oil, or they may be modified oils such as dehydrated castor oil (either blown or unblown), blown linseed oil and alkali isomerized oils prepared from normally non-drying cils such as peanut oil and cottonseed oil, or they may be any other type of unsaturated fatty oil." From U. S. 2,456,671.

Beynon, N. T. (to New Wrinkle, Inc.)

WRINKLE FLEXIBLE MATERIAL WITH RUBBER-SOLUTION COATING. U. S. 2,468,724 (May 3, 1949); C. A. 43, 5608 (1949).

"A 'wrinkling oil' (I), an oil with conjugated double bonds, e.g., tung-, oiticica-, dehydrated castor-, and blown-linseed oil, is mixed with a soln. of synthetic rubber (II) in a suitable solvent, in a ratio of II:I = (10-50):100, a pigment is added in the form of a paste, the mixt. is thinned down with naphtha, and applied by spraying, spreading, or rolling to paper or fabric. The coated material is dried at 130° F. for 30 min. and at 180° F. for 60 min." From C. A.

Blundell, Spence and Co., and Hill, S. AN IMPROVED VARMISH, SPECIALLY APPLICABLE FOR GIVING A FROSTED APPEARANCE TO GLASS, TALC. AND THE LIKE. Brit. 110 (1898) (Nov. 12, 1898); J. Soc. Chem. Ind. 18, 55 (1899). "Three parts of a pale (copal) varnish are warmed with one part of tung oil, with or without the addition of resinates and stearates of lead, manganese, and calcium, and also essential oils." From J. Soc. Chem. Ind.

Bragdon, C. R. (to Ault & Wiborg Corp.) WRINKLE-FINISH ENAMEL AND METHOD OF MAKING. U. S. 2,048,632 (July 21, 1936); C. A. 30, 6221 (1936). "A resin compn. comprising a small amt. of a phenol-formaldehyde resin and a larger amt. of the ester resulting from the almost complete neutralization of abietic acid by glycerol is mixed with raw China wood oil, and the mixt. is heated to about 300° and maintained at about this temp. until the drip from the stirrer strings out to approx. 3 in., a relatively small proportion of linseed oil is added, the batch is quickly cooled to about 230° and maintained at about this temp. until the drip from the stirrer strings out to approx. 2 in.; the batch is then quickly cooled to about 95° and a reducer and pigments are added. The resulting product is suitable for baked enamel coatings." From C.A.

Burgman, G. H. (to G. J. Liebich Co.)

"WRINKLE FINISH" VARNISH.

U. S. 1,934,034 (Nov. 7, 1933); C. A. 28, 662 (1934).

"A base for a wrinkle finish varnish comprises raw China wood oil and a hard fusible resin in a proportion of 5-10% the wt. of the oil, the compn. being heated to 175-285° for 4-8 hrs." From C. A.

Crooks, K. E.

METHOD OF COATING.

U. S. 2,104,637 (Jan. 4, 1938); C. A. <u>32</u>, 1956 (1938).

"A waterproof penetrating liquid compn. contg. China wood oil and which may also contain a liquid hydrocarbon is applied to a dry wood product and the product is dried to gelatinize the China wood oil to form a rough-surfaced coating; over this, there is applied a coating comprising a wax such as carnauba wax together with a solvent, a drier, and coloring matter (the wax used having an affinity for China wood oil) to form a homogeneous coating." From C. A.

Davey, W. P. (to General Electric Co.)

COATING MATERIAL.

U. S. 1,723,844 (Aug. 6, 1929); Paint Varnish Production Mgr. p. 25 (Feb., 1930); C. A. <u>23</u>, 4583 (1929).

"A water japan base is made by methods described in U. S. 1,472,716 utilizing a metallic alkali for saponifying some of the oil in the japan. For example, the japan base may contain: gilsonite 300, rosin 75, boiled linseed oil 150, and boiled chins wood oil 150 parts. To this mixt. are added 7.5 parts of Na₂CO₃ and the procedure of U. S. 1,472,716 carried out. After diln. with hot water and cooling 1-10% but preferably 3.4% of NH₃ is added. Finally water is added to produce the desired diln. and then the coatings of japan are applied by cataphoresis. Reference is made also to U. S. 1,294,627." From Paint Varnish Production Mgr.

Drummond, F. E. (to New Wrinkle, Inc.)

PROCESS OF PRODUCING RAPID-DRYING COATING COMPOSITIONS. U. S. 2,381,653 (Aug. 7, 1945); C. A. <u>39</u>, 5097 (1945).

"The drying of a coating to produce either a smooth surface or a wrinkle finish can be controlled by varying the amt. of compds. present having conjugated double bonds of the general formula (-CH=CH-), where x is equal to 2, 3, or 4. For producing a nonwrinkling oil vehicle a drying oil, such as linseed, is mixed with varying amts. (depending on the type of oil used) of a fat acid triglyceride compd., where x is equal to 2. For producing a wrinkling-oil vehicle a fat acid triglyceride compd. is used, where x is equal to 3 or more. In both prepns. the mixts. are heated to 350-450°F. for 1/2 to 1 hr. Preferably triglycerides are used, but diglyceride or fatty acids alone when a sufficient amt. of glycerol is present, may be employed. Drying oils or semidrying oils may be used either in the raw state, refined, or in blown condition. Natural or synthetic resins and driers may be incorporated." From C. A.

Two examples are given in which x equals 3 in the formula $(-CH=CH-)_x$, These are triglyceryl eleostearate and triglyceryl licenate. Examples of non wrinkling oils are: (Example 7) China-wood oil, 40-60%, with triglyceryl isolinoleate, 60-40; (Example 8) China-wood oil, 40-60, with triglyceryl isolinolenate, 60-40. Examples of wrinkling oils are: (Example 9) linseed oil, 5-25, with triglyceryl eleostearate, 95-75; (Example 12) perilla oil, 5-25, with triglyceryl eleostearate, 95-75; (example 15) soya bean oil, 5-20, with triglyceryl eleostearate, 95-80.

Drummond, F. E., and Waldie, W. A. (to New Wrinkle, Inc.) METHOD OF FINISHING ARTICLES.

U. S. 2,283,420 (May 19, 1942); C. A. 36, 6364 (1942).

"To produce a hard wrinkle finish, the surface of an article is thoroughly cleaned and a costing compn. is applied contg. wrinkle drying oil, and the coating film is subjected to infrared radiation of between 7200 and 14,000 A. for 5-15 min. to initiate wrinkling of the film surface, and drying is then effected by infrared radiation of over 14,000 A. in a current of air to set the film to a hard wrinkle finish." From C. A.

Drummond, F. E., and Waldie, W. A. (to New Wrinkle, Inc.). WRINKLE-FINISH DRYING COMPOSITIONS.

U. S. 2,373,177 (Apr. 10, 1945); C. A. 39, 3167-8 (1945).

"Wrinkle finishes are produced which contain a substantial portion of dehydrated castor oil in place of China wood oil, which can be compounded with pigments, and which are harder and more rapid drying. Resin, wrinkling drying oil other than dehydrated castor oil and metallic drier are mixed and the resulting varnish blended in equal proportions with a second wrinkling oleoresinous varnish contg. dehydrated castor oil. The dehydrated castor oil may be modified by treating with glycerin and phthalic anhydride. By modifying the drier, dehydrated castor oil may wholly replace China wood oil." From C. A.

Fey, Georg, & Co.

PROCESS FOR THE PRODUCTION OF A FLAT-DRYING VARNISH CONTAINING NITROCELLULOSE.

Swiss 132,318 (Apr. 15, 1929); C. A. 23, 5051 (1929).

"Nitrocellulose varnish is caused to dry with a mat surface by adding vegetable oil. Thus, a varnish contg. pyroxylin, AcOBu, BuOH, C₆H₆, alc., softening material and resin is given a mat drying surface by addn. of wood oil." From C. A.

Kronstein, Abraham

PROCESS FOR PRODUCING CERTAIN EFFECTS IN PAINTS AND VARNISHES. Fr. 398,604 (Mar. 27, 1909).

A silky appearance can be obtained by drying a composition of "l'huile de goudron de bois chinoise" in sunlight and in a current of air.

Kronstein, Abraham

PROCESS FOR PRODUCING A SILK-LIKE EFFECT IN PAINTS. Austria 49,169 (July 25, 1911).

This specification, like that of French Patent 398,604 (Kronstein), refers to the production of a silk-like appearance produced in wood oil paints and varnishes by drying them in a stream of moving air.

Kummel, Paul

PREVENTING FILM FORMATION ON OIL LACQUERS AND ON SYNTHETIC RESIN LACQUERS.

Ger. 714,604 (Aug. 20, 1938); C. A. <u>38</u>, 1894 (1944).

"The last runnings of turpentine distn., essentially having a b.p. 170-200°, are used for preventing films on lacquers and lac dyes having a base of drying oil, drying synthetic resin or a mixt. of both." From C. A.

"This film formation occurs in all oil, tung oil, alkyd resin lacquers.etc." From the patent.

Luáces, E. L. (to New Wrinkle, Inc.)

WRINKLE COATING COMPOSITION.

U. S. 2,465,243 (Mar. 22, 1949); C. A. 43, 5206 (1949).

"A wrinkle coating compn. prepd. by allowing to react at 400°F., glycerol 60, phthalic anhydride 120, fatty acid 102 parts, 0.5 to 3% top drier (Co naphthenate), and hydrocarbon diluent. Fat acids are from treatment of cotton seed, corn, or peanut oil with alc. soln. of Na ethylate under reflux sufficient to cause rearrangement of the nonconjugated double bonds and formation of fat acid soaps." From C.A.

The desirable characteristics of tung, and other oils, are discussed in relation to their conjugated structures and to their processing. Their high prices, nonuniformity, and variable availabilities have led to the development of substitutes.

Luáces, E. L. (to New Wrinkle, Inc.)

UNCOOKED WRINKLE COMPOSITION CONTAINING SYNTHETIC RUBBER AND CONJUGATED-DOUBLE-BONDED OIL.

U. S. 2,468,989 (May 3, 1949); C. A. <u>43</u>, 5972 (1949).

"The cooking may be omitted in making a wrinkle finish contg. an elastomer (I). An example comprises I (butadiene-styrene, butadieneacrylonitrile, neoprene, or polyvinyl chloride) 40, wrinkling oil (II) 100, pigment paste (pigment 2/3, II 1/3) 60, and naphtha 10 parts. II is admixed with a soln of I in the ratio II 10-50, I 100; solvents for I are listed as excellent or fair to good, and diluents are specified. (II may be tung, oiticica, dehydrated castor or alkali isomerized linseed oil). Texture of the wrinkle pattern is a function of the type and amt. of I." From C. A. Luáces, E. L. (to New Wrinkle, Inc.)

WRINKLE DRYING COMPOSITION CONTAINING DEXTRAN BENZYL ETHER. U. S. 2,490,070 (Dec. 6, 1949); J. Am. Oil Chemists' Soc. <u>27</u>, 111 (1950).

"A wrinkle drying coating composition consists of 100 parts of a wrinkling oil, 10-50 parts of dextran benzyl ether, and a thinner, admixed at room temperature." From J. Am. Oil Chemists' Soc.

"Wrinkling oils are oils which include conjugated double bonds in their chemical structure. They may be native oils such as tung and oiticica oil, or they may be modified oils ---" From the patent.

Moore, H. R. (to New Wrinkle, Inc.)

METHOD OF PRODUCING A RESIN.

U. S. 2,154,954 (Apr. 18, 1939); C. A. 33, 5686 (1939).

A method of making a wrinkling resin varnish involves mixing vegetable drying oils including tung oil and nonfrosting drying oil fatty acids with glycerin and a primary resin of the group consisting of rosin modified and ester-gum modified phenol-CH₂O condensation products, treating the mixt. at a temp. of about 250° for approx. 15-25 min. and thereafter incorporating phthalic anhydride and continuing the polymerization at a temp. of about 225°, and thereafter blowing with air to aerate the product.

Root, F. B. (to Flood & Conklin Co.) WRINKLING FINISH.

U. S. 1,689,892 (Oct. 30, 1928); C. A. 23, 293 (1929). "China wood oil 7-17 gals. is mixed with a "wrinkle finish resin" 100 lbs. using oil at least most of which has been preoxidized by blowing, and with a drier and thinner." From C. A.

Root, F. B. (to Flood & Conklin Co.) WRINKLING FINISH.

U. S. 1,732,661 (Oct. 22, 1929); C. A. 24, 252 (1930).

"Surfaces are provided with a wrinkled baked coating of a drying oil and a resin e.g., China wood oil and Congo resin. Various auxiliary ingredients also are added." From C. A.

Root, F. B. (to Chadeloid Chemical Co.)

WRINKLE FINISH COATING.

U. S. 1,883,408 (Oct. 18, 1932); C. A. <u>27</u>, 1217-8 (1933).

"A coating compn, is used comprising a 'wrinkling oil' such as perilla or linseed oil, a 'wrinkle finish' resin and a drier and thinner in suitable proportions, and drying is effected at a temp. which produces a wrinkle finish. Numerous details and examples are given." From C. A.

The use of "China wood oil, blown China wood oil and partially oxidized or pre-oxidized China wood oil" is discussed in detail.

Waldie, W. A.

IMPROVEMENTS IN COATING COMPOSITIONS AND METHODS OF MAKING THE SAME. Brit. 523,526 (July 16, 1940); C. A. <u>35</u>, 6474 (1941).

"A mixt. contg. raw. wrinkling oil, resin and a drier is heated until a homogeneous mixt. is produced. It is suddenly chilled or cooled by the application of cold H₂O or refrigeration. The heat treatment is between 450 and 550°F.⁵ The metallic drier, linseed oil and portion of the resin are added after heating the mixt. Baking the finish accentuates the wrinkling." From C. A.

Raw China wood oil and blown China wood oil are included in the list of wrinkling oils.

Waldie, W. A.

PASTE COMPOSITION IN COMPOUNDING WRINKLE-FINISH ENAMELS. Brit. 523,527 (July 16, 1940)*; C. A. 35, 6474 (1941).

"Different wrinkle textures are obtained by incorporating into a varnish various amts. of a paste contg. a noncoloring filler such as asbestime. The varnish comprises a raw wrinkling oil and a bodied drying oil such as linseed oil." Other fillers can be used such as whiting, MgCO₂, diatomaceous earth and china clay. The essential step in making the varnish is the sudden chilling or cooling after heating the China wood oil and resin to about 540°F." From C. A.

Waldie, W. A. (to New Wrinkle, Inc.)

PAINT VEHICLE.

U. S. 2,268,002 (Dec. 30, 1941); C.A. <u>36</u>, 2743 (1942).

"A wrinkle-drying coating compn, is formed with use of a vehicle comprising raw China wood oil, bodied drying-oil resin, a metallic drier, a solvent thinner, and 2-5% of a wrinkle texture-modifying compn. comprising fatty acids of China wood oil or linseed oil dissolved in a solvent." From C. A.

Waldie, W. A. (to New Wrinkle, Inc.)

PIGMENT PASTE.

U. S. 2,275,239 (Mar. 3, 1942); C. A. <u>36</u>, 4360 (1942).

"A fine-textured wrinkling enamel comprises an inert paste consisting of a grinding vehicle and a pigment which may be asbestine or a mixt. of MgCO₃ with diatomaceous earth, a color pigment and a cooked wrinkling varnish base comprising the following formula: modified phenolaldehyde resin 100 lb.; a drier selected from the group consisting of lead acetate and linoleate 5 to 9 lb.; raw China-wood oil 5 to 25 gal.; vegetable drying oil selected from the group consisting of bodied linseed oil, bodied perilla oil and bodied citicica 2 to 20 gal., solvent naphtha 8 to 10 gal., and toluene 18 to 25 gal., the inert paste imparting the fine wrinkle qualities to the resulting finished enamel." From C. A.

Waldie, W. A. (to New Wrinkle, Inc.)

WRINKLE-FINISH COMPOSITION AND METHOD OF MAKING

U. S. 2,294,703 (Sept. 1, 1943); C. A. <u>37</u>, 1052-3 (1943).

"A wrinkle-finish compn. is prepd. by: (a) mixing 1/4 to 3/4 of the total amt. of resin to be used of the total amt. of a wrinkle oil selected from the class consisting of raw China-wood oil, raw oiticica oil, and raw poyok oil, together with heat-bodied linseed oil, and heating to 450°F. to 540°F.; (b) adding a metallic drier; (c) adding the remainder of the resin and dissolving it in the mixt.; (d) rapidly chilling the liquid without the use of thinners, and adding thinners to produce a spray varnish having low viscosity and good spray qualities." From C. A. Waldie, W. A. (to New Wrinkle, Inc.)

METHOD OF PREPARING WRINKLE COMPOSITIONS.

U. S. 2,347,303 (Apr. 25, 1944); C. A. 32, 206 (1945).

"A coating compn. to produce wrinkle finish is prepd. from modified phenol aldehyde resin ("Amberol" or "Beckacite") 100, Pb acetate or linoleate 5-9 lb., raw china-wood oil 15-25, bodied linseed, perilla or oiticica oil 2-20, solvent naphtha 8-10 and toluene 18-25 gal. The bodied oil employed instead of blown oil is previously heat-treated and offers the advantage of stability of the final product. Other resins may be used instead of the above-mentioned, such as kauri, dammar, Congo or Cumar. The method of making the varnish-base compn. is similar to that used with blown oils. To make a clear wrinkle compn. 2-5% of a liquid drier (I) is added to it, oil fat acids 8-10 lbs., toluene, xylene, or coal-tar solvent 6-8 gals. This addn. is called the "top" drier and incorporated into the varnish base constitutes a wrinkle-finish coating which may be baked at lower or higher temps. according to its use on metallic surfaces, wood, paper, etc." From C. A.

Waldie, W. A. (to New Wrinkle, Inc.)

METHOD OF PREPARING WRINKLE COMPOSITIONS.

U. S. 2,347,304 (Apr. 25, 1944); C. A. <u>39</u>, 206 (1945).

"Linseed oil fatty ecids and a solvent for them modify the texture of wrinkle finishes. The use of China wood oil acids is illustrated in examples but is not covered by the claims. This patent is related to U. S. 2,347,303." From C. A.

Waldie, W. A. (to New Wrinkle, Inc.)

METHOD OF MODIFYING THE TEXTURE OF COATING COMPOSITIONS.

U. S. 2,414,006 (Jan. 7, 1947); C. A. 41, 2915 (1947).

"The texture of a wrinkle-finish costing compn. is controlled by adding drying-oil fat acids, e.g., the acids of china wood oil or linseed oil, together with a solvent for the acids. The higher the proportion of acid added, the finer will be the texture of the wrinkle finish." From C. A.

Waldie, W. A. (to New Wrinkle, Inc.)

FLEXALIZER.

U. S. 2,437,369 (Mar. 9, 1948); C. A. 42, 4371 (1948).

"A mixt. (I) (1 part) of a drying oil (10-20 gal.) having one or more conjugated double bonds, a nondrying oil (10-20 gal.) preferably blown castor oil (II), and a drier (0.5-1.5 lbs.), such as Co, Pb, or Mn acctate or oxide, added to a wrinkle varnish (3-9 parts) produces a flexible wrinkle varnish suitable for oilcloth, etc. Thus I is prepd. by heating 4 gal. II and 16 gal. raw tung oil at 540°F. until the mixt. is about to gel, adding 12 gal. II, heating to 450°F., adding 1 lb. Co(OAc)₂ and heating at 500°F. until the mixt. is homogeneous." Weldie, W. A. (to New Wrinkle, Inc.)

AIR DRYING WEINKLE FINISH.

U. S. 2,455,541 (Dec. 7, 1948); C. A. 43, 2448 (1949).

"Air-drying wrinkle finishes are prepd. from short-oil varnish (I) and oil dryer (II) contg. 30-130 gal. II per 100 gal. of I. I is made by heating 2-15 gal. conjugated double-bonded drying oil (III) with 100 lb. of rosin-modified phenol-HCHO resin to 500-540°F. This is cooled to 350°F., and the necessary hydrocarbon solvents are added. II is formed by treating at 500°F. 8-10 lb. Co and (or) Pb resinates with 10-20 gal. III, cooling and adding solvents. III may be raw tung, liquefied oiticica, or other similar oils or mixts. of them." From C. A.

Williams, G. M. (to New Wrinkle, Inc.)

POLYMERIZATION NUCLEUS FOR WRINKLING OILS.

U. S. 2,428,901 (Oct. 14, 1947); C. A. 42, 388 (1948).

"Organometallic compds. and metallic ions (Groups I, II, and III in periodic table) are treated with drying oils to establish polymerization nuclei which will increase the drying rate of the oil and develop their wrinkle-forming characteristics. Soybean oil (100 g.) is placed in a closed container and blanketed with N_2 . The oil is cooled to 0° and 0.05 g. of metallic Na added. The mixt. is stirred and allowed to warm to room temp. slowly. When no further reaction is evident, the oil is heated to 120° and held at that temp. for 30 min. with continuous agitation. The resulting product may be employed in the usual manner for producing wrinkle varnishes." From C. A.

The differences in drying characteristics between tung oil (Chinawood oil) and other oils such as linseed oil is largely due to the fact that the former by virtue of its high degree of conjugation and symmetry is able to form a closely knit three dimensional polymerized nucleus. Linseed oil and other similar oils, on the other hand, form drawn out polymerized units which are comparatively loosely knit.

.

.

•

~ /

· · ·

2494