

PAINT, VARNISH, AND LACQUER INDUSTRY IN GERMANY. H. O. Farr (Joint Intelligence Objectives Agency). *Paint Oil Chem. Rev.* 109, No. 11, 5-7, 42-43 (1946). Part II., *ibid.*, No. 12, 13, 14, 16, 18, 43-44 (1946).

SOME EMPIRE DRYING OILS. G. T. Bray (Imperial Institute). *Paint Tech.* 11, No. 123, 97-101, 122 (1946). A review of the production and properties of drying oils produced in the British Empire; 26 references.

WOOD OIL SITUATION IN CHINA AND DIFFICULTIES AFFECTING IT AS REVIEWED BY AN EXPERT. S. C. Wood (Universal Trading Corp., New York). *Paint Oil Chem. Rev.* 109, No. 11, 13, 20 (1946).

ARTIFICIAL TUNG OIL. T. P. Hilditch and M. L. Meara (Univ. Liverpool). *Chemistry & Industry* 1946, 158. A commercial product, "Trienol," alleged to be a synthetic tung oil, was examined and found to contain over 60% of  $\alpha$ -eleostearic acid. Since the production of the extremely labile  $\alpha$ -form of eleostearic acid is not possible in synthetic operations in which high temperatures and chemical reagents are employed and is confined to eleostearic glycerides produced by the living seed, it follows that the sample in question could not have been produced synthetically.

THE EFFECT OF LIPOXYDASE ON THE OXIDATION OF ELEOSTEARIC ACID. H. Sullmann (Lab. der Univ.-Augenlinik, Basel, Switzerland). *Helv. chim. acta.* 27, 789-93 (1944). Contrary to the previous findings of Summer, lipoxylase is found to accelerate the oxidation of eleostearic acid. The acceleration occurs during the early stages of oxidation; in later stages,  $O_2$  uptake is less in the presence of the enzyme. Inactivated lipoxylase appears to inhibit the oxidation of eleostearic acid.

APPLICATION OF RAMAN SPECTRA TO THE STUDY OF FATTY MATERIAL. CONSTITUTION OF SOME UNSATURATED ACIDS. G. Dupont and F. Yvernaud. *Bull. Soc. Chim.* 12, 84-7 (1945). Raman spectra are obtained for the Me ester fractions prepared by alcoholysis of butter, castor oil, and poppy oil. From the position of the  $C=C$  line it is concluded that oleic acid has the *cis* configuration while elaidic acid has the *trans* configuration. Linoleic and ricinoleic acids are *cis*. The  $C_6$  and  $C_8$  fractions from butter give Raman lines corresponding to a  $C\equiv C$  bond. The  $C_{10}$  acid from distilled castor oil has the triple bond line as well as a line indicating the presence of a terminal double bond. (*Chem. Abs.* 40, 3055.)

THE USE OF LOW-TEMPERATURE CRYSTALLIZATION IN THE DETERMINATION OF COMPONENT ACIDS OF LIQUID FATS. II. FATS WHICH CONTAIN LINOLENIC AS WELL AS LINOLEIC AND OLEIC ACIDS. F. D. Gunstone and T. P. Hilditch (Univ. Liverpool). *J. Soc. Chem. Ind.* 65, 8-13 (1946). The analysis of fatty acids containing saturated oleic (*I*), linoleic (*II*), and linolenic (*III*) acids is discussed. The application of low-temperature crystallization for the preliminary separation of these acids in mixtures containing only

*I* and *II* besides saturated acids has been described by Hilditch and Riley [cf. *Oil & Soap* 21, 341 (1945)]. If *III* is also present, the acids are isomerized with alkali and then determined spectrophotometrically. For precise accuracy, G. and H. propose to separate the mixed fatty acids into several groups by crystallization from appropriate solvents at low temperatures and then, after isomerization with alkali, spectrophotometrically determine the quantity of individual acids in each group. Mixed fatty acids from "drying" type oils are crystallized from acetone (5 cc. per g. of fatty acids) at  $-50^\circ$  (oils with an I value below 160 are first crystallized at  $-30^\circ$  and the filtrate is then cooled to  $-50^\circ$ ). The solution obtained is rich in *II* and *III*. The combined solids from  $-30^\circ$  and  $-50^\circ$  are again crystallized from acetone (5 cc. per g.) at  $-30^\circ$ . The "soluble in acetone at  $-30^\circ$ " consists of acids rich in *II* and *III*. The acids deposited in this crystallization are finally crystallized from ether (10 cc. per g.) at  $-30^\circ$ . Solids low in I value are deposited and the "soluble in ether at  $-30^\circ$ " is a mixture of saturated acids *I*, *II*, and *III*, with *I* usually predominating. Each crystallization requires at least 4-5 hours. Solvents and temperatures may be varied in each case. The proportions of *II* and *III* in each of the groups, after isomerization with alkali in ethylene glycol at  $170^\circ$  for 15 minutes in one portion and at  $180^\circ$  for 60 minutes in another portion, are determined from the extinction coefficients of the absorption bands at 268  $m\mu$  and 234  $m\mu$ . The quantities of *I* and of saturated acids are calculated from the I value of the original mixture. Thus the composition of the total fatty acids in terms of *I*, *II*, *III*, and saturated acids is established. Saturated acids are determined in another operation. Hydrogenated Me esters of the original fat acids are fractionally distilled. The lower fractions are collected until the saponification equivalent of the distillate closely approaches that of Me stearate. The fractions are calculated as mixtures of palmitate and stearate. The final high-boiling fraction, if any, and the undistilled residue are analyzed for unsaponifiable matter. Since in addition to the spectrophotometrical data of the amounts of unsaturated  $C_{18}$  acids and of saturated acids, the proportions of palmitic acid and unsaponifiable matter are now fixed, the stearic acid can be calculated by difference. Higher saturated acids (arachidic acid) are determined separately by fractional distillation of the esters of the least soluble group of acids obtained by low-temperature crystallization. A second method for the determination of the saturated acids is mentioned in which, without hydrogenation, the Me esters of each group of the separated acids are fractionally distilled. However, this procedure requires much more time and gives less accurate results. In a critical discussion of the new method it is said that the spectrophotometrical determination of *II* and *III*, applied to acids obtained by low-temperature crystallization, is more reliable than any method previously used. The analysis of the saturated acids by fractional distillation of the hydrogenated methyl esters is also considered

as more satisfactory than the lead salt separation method. The procedure is illustrated in a few samples. Composition of linseed oil acids, I value 191.3; palmitic 7, stearic 8, arachidic 1, oleic 13, linoleic 17, and linolenic 54% by weight; wheat germ oil acids: palmitic 16, stearic 6, oleic 12, linoleic 57, and linolenic 9% by weight; Ceylon rubber-seed oil acids, I value 139.8: palmitic 11, stearic 12, arachidic 1, oleic 17, linoleic 35, and linolenic 24% by weight; Nigerian rubber-seed oil acids, I value 141.0: palmitic 9, stearic 10, arachidic 1, oleic 20, linoleic 39, and linolenic acid 21% by weight. The prospects of rubber-seed oil as a drying oil are also discussed. (*Chem. Abs.* 40, 3007-9.)

**PEROXIDATION IN RELATION TO OLEFINIC STRUCTURE.** E. H. Farmer (Brit. Rubber Producers' Research Assoc., Welwyn Garden City, Herts). *Trans. Faraday Soc.* 42, 228-36 (1946). The autoxidation of olefinic substances comprises 2 major phenomena: that of the incorporation of molecules of  $O_2$  (peroxidation) and that of secondary change (peroxide breakdown). When the peroxido-olefins are at least moderately stable, no serious difficulty attends the study of their decomposition. When however, they are unstable, deductions of their structure and mode of decomposition must be made from the nature of the secondary decomposition products actually isolated, and hence erroneous conclusions may easily be drawn. All peroxides of conjugated non-aromatic dienes and polyenes are formed by addition of  $O_2$  to the double bond system, even if this system is flanked by  $-CH_2-$  groups as is the case with Me sorbate and Me eleostearate. Even when of high thermal stability they exist as polymeric bodies rarely exceeding octameric complexity and containing little or no monomeric component. They undergo chemical reduction and catalytic hydrogenation so incompletely that no satisfactory absolute method of their analytical determination exists. Catalytic hydrogenation fails to yield quantitative reduction to monomeric 1,4-diol because the metal surface promotes extensive catalyzed decomposition. Thus methyl eleostearate yields 60% of mixed hydroxyketo and dihydroxystearic esters. Crude polymeric peroxides formed from open-chained conjugated systems usually contain up to 20% of oxidative scission products, which may occur unavoidably during absorption of  $O_2$  or otherwise may first occur by metal catalyzed decomposition during hydrogenation. Sorbic ester,  $\alpha,\delta$ -diphenylbutadiene, and Me eleostearate belong to the spontaneous unavoidable type while  $\beta,\gamma$ -dimethylbutadiene and isoprene are of the catalyzed type. Numerous polynuclear aromatic compounds form photo-oxides which dissociate thermally into the original hydrocarbon and  $O_2$ . Di- and polyolefinic compounds containing the 1,4-system form hydroperoxides upon the methylene groups between the double bonds. The detachment of an H-atom during the oxidation enables the radical to rearrange into more stable conjugated forms. Mono-olefinic compounds oxidize less easily, but appear to behave in a very similar manner. In mono-olefinic systems the point of attachment follows the ordinary directive rules for ethylenic reactivity. Good justification appears to exist for postulating universal initiation of autoxidation by addition. The  $\alpha$ -methylene products from uncon-

jugated olefins follow by an intermolecular chain mechanism. The influence of peroxidic structure upon the tendency to chain scission is obscure since the course of reaction is much affected by experimental conditions. The polymeric tendency referred to in connection with Me eleostearate and conjugated olefins is of general occurrence and appreciable polymer fractions are found in even the most favorable cases of hydroperoxide formation. Finely divided metals actively promote a type of decomposition which differs from the spontaneous decompositions and is characterized by the formation of  $=C=O$  and  $\equiv C-OH$  groups.

**DRYING OIL EMULSIONS WITH ZINC OXIDE AS SUBSTITUTES FOR STRAIGHT DRYING OILS.** V. S. Varlamov. *Pishchevaya Prom.* 1945, No. 2, 24-7. With Pb-Mn driers as emulsifiers and ZnO as stabilizer, O-W emulsions of linseed oil were prepared, for example, oil (acid No. 4.4) 50, water 49.7, ZnO 0.3%. The drier contained Pb 0.1 and Mn 0.07%. This emulsion had 4.5 times the viscosity of the raw oil and was stable over a 65-day test period. A similar emulsion but with linseed oil of acid number 9.9 and a drier containing Pb 0.12 and Mn 0.08% showed after 18 days only traces of phase separation attributable to evaporation of water. For use as paints these emulsions were successfully pigmented with ZnO, lithopone, whiting, Cr oxides, chrome green, litharge, red Pb, and hematite. Yellow ochre, ultramarine and powdered silica gel were not readily compatible with these O-W emulsions. Economy in linseed oil for 2 paint coats is 27% (ZnO pigment) or 24% (hematite pigment) as compared with straight oil paints. In a single coat the saving is greater. (*Chem. Abs.* 40, 3621.)

## PATENTS

**SYNTHETIC DRYING OIL.** C. J. Mighton (E. I. du Pont de Nemours and Co.). *U. S.* 2,401,769. A synthetic drying oil comprises a copolymer of furylaldehyde (35-5%) and a drying or semidrying oil (65-95%).

**PAINT COMPOSITION.** M. T. Schmidt (U. S. Gypsum Co.). *U. S.* 2,401,666. A paint consists of a drying oil, a reaction product of an aliphatic fatty acid having 12-24 C atoms with a volatile alkaline reacting material, 4% of coal tar solvent, pigment, and fillers. Coal tar naphtha may be used as the coal tar solvent.

**SYNTHETIC DRYING OILS AND COATING COMPOSITIONS.** E. I. du Pont de Nemours and Co. *Brit.* 574,680. Glycerine is partially esterified with an  $\alpha,\beta$ -ethylenic- $\alpha$ -(alken-1-yl) monofunctional acid, such as  $\alpha$ -vinylcinnamic, or  $\alpha$ -vinylcrotonic acid, and esterification is then completed with an aliphatic monocarboxylic acid such as oleic, stearic, lauric, crotonic, and sorbic acids or the fatty acids of vegetable oils. Films of the mixed glycerides when mixed with driers dry in 8 hours at room temperature to hard, clear, light-colored, tack-free films. The glycerides may be blended with natural resins and synthetic resins of various types.

## CORRECTION

ABSTRACT TITLED LALLEMANTIA OIL (Steger and van Loon), *Oil & Soap* 22, 175 (1946), last line should read "linolenic acid 53.5%."