ABSTRACTS . . . . Don Whyte, Editor

• Oils and Fats

R. A. Reiners, Abstractor

The equilibrium moisture content of tung fruit and its components at different relative humidities. R. L. Holmes, R. S. McKinney and J. C. Minor (U. S. Tung Oil Lab., Bogalusa, La.). *Proc. Am. Tung Oil Assoc.* **1950**, 24-36. The equilibrium moisture contents at 25° at 9 different relative humidities were determined for whole tung fruit and its component parts and on the cake from continuous screw presses. The average relative humidity of the tung-growing area is about 75% and at this humidity the equilibrium moisture contents are: whole fruit, 12.4; outer hull, 19.3; inner hull, 14.7; shell, 12.3; kernels, 6.1; seed, 8.2; and press cake, 10.3%, respectively. (*Chem. Abs.* **45**, 3620)

Comparison of the whole fruit and component methods of analysis of tung fruit. F. C. Pack, R. L. Holmes and R. S. McKinney (U. S. Tung Oil Lab., Bogalusa, La.). *Proc. Am. Tung Oil Assoc.* **15**, Pt. 2, 25-30(1949). No differences were found in the oil content of tung fruit when ground in a Bauer laboratory mill with plate spacings from 0.004 in. to 0.012 in. but the results were lower with spacings of 0.020 in. The average percentages of moisture obtained by the methods differ enough so that calculations on a moisture-free basis give apparent differences in oil content. Both the whole-fruit and component method yield reliable results over a wide range of moisture content, although with the component method, kernels with more than 10% moisture must be partially dried before regrinding for reextraction. (*Chem. Abs.* **45**, 3620)

Grape-seed oil. K. Ishimaru (Inst. Phys. Chem. Research, Tokyo). *J. Agr. Chem. Soc. Japan* **18**, 651-4(1942). The ethyl ether extract of the grape seed was 9-13% in 4 varieties. The petroleum ether-extracted grape-seed oil had d^{20} 0.900-0.977, n_{20} 1.4718-1.4765, η at 50° 0.7-19.3, saponification value 174-196, iodine value 28-34 (very low compared to the literature values 125-157), SCN value 2.9-7.9, Reichert-Meissl value 0.54-1.0, Polenske value 2.2-3.9, Hehner value 95.2-95.8, and acetyl value 19.8-41.2. (*Chem. Abs.* **45**, 3618)

The composition of the seed and funicle oils of Acacia cyclops. M. M. Black, D. A. Harris and H. M. Schwartz (Univ., Cape Town). *J. S. African Chem. Inst.* **2**, 111-18(1949). Data for solvent extracted funicle oil and solvent extracted seed oil of *Acacia cyclops* are as follows: color deep red, greenish yellow; yield 40, 10%; d^{25} 0.917, 0.922; n^{25} 1.4691, 1.4746; saponification no. 188, 186; iodine no. 72, 137; acid no. 3, 2; unsaponifiable matter 2.78, 0.99%. The fat acid composition in percentage was: lauric 0.5, 0.1; myristic 0.3, 0.7; palmitic 21.6, 5.6; stearic 2.7, 0.6; arachidic 0.4, 0.8; C_{22}-C_{24} saturated ---, 2.9; tetradecenoic 0.9, ---; hexadecenoic 7.3, 8.6; oleic 61.7, 10.1; linoleic 3.1, 67.7; linolenic 0.3, 0.8; C_{20} unsaturated 1.2, 2.1. (*Chem. Abs.* **45**, 3616)

Films of hydrocarbon-stearic acid mixtures. H. Sobotka and Shirley Rosenberg (Mt. Sinai Hosp., New York, N. Y.). *J. Colloid Sci.* **5**, 581-5(1950). Mixed films of stearic acid with $C_{18}H_{38}$, $C_{28}H_{58}$, or $C_{36}H_{74}$ on an aqueous solution containing Ba acetate and $KHCO_3$ and as built-up monolayers were prepared with different proportions of acid and hydrocarbon. Stable films were formed only when the molecular ratio of hydrocarbon to acid was 1:2 or less. (*Chem. Abs.* **45**, 3616)

Films of omega-branched fatty acids. H. Sobotka, Shirley Rosenberg and A. Birnbaum (Mt. Sinai Hosp., New York, N. Y.). *J. Colloid Sci.* **5**, 567-80(1950). n-Alkyl fat acids are compared with fat acids having terminal isopropyl or tert-butyl groups with respect to the properties of their insoluble monolayers on aqueous solutions. The surface pressure-area relations were measured at 18° for C_{16}, C_{18}, C_{20}, C_{22}, and C_{24} fat acids of the above 3 structures. The molecular areas of the branched-chain acids are greater than those of their normal isomers at any given pressure. The branched-chain acids resemble the normal acids in built-up film properties, with the important exception that the branched-chain acids have an enormous surface volatility. Molecular sublimation of these acids across layers of stearic acid several hundred A. thick was observed. (*Chem. Abs.* **45**, 3616)

Determination of peroxide value of rancid fats—a modified procedure. S. Mukherjee (Coll. Sci., Calcutta). *J. Indian Chem. Soc.* **27**, 87-90(1950). The methods of Wheeler and Lea are combined. Flush the reaction vessel and fat solvent for 3-5 and 5-10 min., respectively, with CO_2 to exclude air. Weigh 1 g. fat into a 750-ml. glass-stoppered bottle. Add 10 ml. solvent consisting of chloroform (40%) and acetic acid (60%). Add 2 ml. saturated aqueous KI and place the vessel in the dark 1 hr. at 36-37°. Dilute the reaction mixture with O_2-free distilled water and titrate with 0.005 N aqeuous $Na_2S_2O_3$. (*Chem. Abs.* **45**, 3615)

Extraction of vegetable oils by the method of compression. Extraction of vegetable oils by solvents. P. G. Garoglio. *Tecnologia de los acietes vegetales.* **1**, 769-866. A review.

The determination of fat in foods. W. Stoldt (Nahrungsm. Unters. Amt., Kiel, Germany). *Deut. Lebensm. Rundschau* **47**, 13-15(1951). For the determination of total fat it is necessary to treat the material first with a mixture of 60 cc. HCl (1.19) and 100 cc. water. The solution is filtered and the filter paper and fat are dried and extracted with ether. The latter is evaporated and the residue dried and weighed as total fat. This method and the direct extraction methods in use were applied to a number of dairy products and cocoa, and comparative results tabulated. (*Chem. Abs.* **45**, 3522)

The simple and rapid determination of saponification numbers. F. L. Hahn (Univ. nacl. auton. Mex., Mexico, D. F.). *Anal. Chim. Acta* **4**, 577-9(1950). KOH dissolved in a 1:1 mixture of Cellosolve and xylene is an ideal reagent for the determination of saponification numbers. (*Chem. Abs.* **45**, 3281)

A rapid test for castor oil in soaps and lipsticks. Sister M. Clarita Mangold (Rosary Hill College, Buffalo, N. Y.). *J. Chem. Ed.* **28**, 266(1951). About 1 g. soap or lipstick are placed in test tube with 3 pellets NaOH and heated gently until heavy white fumes are formed. The odor of octyl alcohol indicates the presence of castor oil. As little as 10% castor oil can be detected.

Bacterial components of Corynebacterium diphtheriae. I. Studies of fats. 1. M. Asano and H. Takahashi (Inst. Infectious Diseases, Tokyo). *J. Pharm. Soc. Japan* **63**, No. 3A, 17-19 1945). The lipids of *Corynebacterium diphtheriae* were separated by acetone extraction into fats and phospholipids. The presence of the following fatty acids in the acetone soluble fraction was demonstrated: palmitic, myristic, behenic, lignoceric, palmitooleic, myristooleic, heneicosenic, octacosenic, and diphtheric. (*Chem. Abs.* **45**, 3906)

Fractionation of vegetable oils. H. Farr. *Oil Colour Trade J.* **114**, 729, 730, 732, 734, 736(1948). Solvent segregation with furfural, of soybean, linseed, and fish oils is described. (*Chem. Abs.* **45**, 4065)

Rice Oil. I. Acid decolorizing. H. Sakurai (Osaka Univ.). *J. Chem. Soc. Japan*, Ind. Chem. Sect., **52**, 193-4(1949). Decolorization of rice bran oil by aeration with use of H_2SO_4 and a catalyst was studied. The oil used had an acid value 25, saponification no. 178, iodine no. 70, acetyl no. 22, $[\alpha]^{15}$ 0.9266, $n^{15.5}$ 1.4738. A mixture of 10 cc. of the oil and 10 cc. of H_2SO_4, HCl, or oxalic acid is agitated by air for 3 hrs. at 90-95°. Decolorization is observed with use of 0.5% H_2SO_4 or HCl in 30 minutes and of 10% oxalic acid in 3 hrs. Prolonged aeration causes coloration. When H_2 is used in place of air, similar results are obtained.

II. Refining of rice oil. *Ibid.* 247-8. In refining a series of rice bran oils having acid values from 21 to 70, a treatment using both acid and alkali gave good results, with yields 78-45%, acid values 2-19, and improved color. A mixture of 100 g. oil and the same volume of 0.5% HCl was agitated by air for 30 minutes at 70 ± 5°. After separating the water layer, a 15% solution of NaOH or Na_2CO_3 with 20% excess in proportion to the acid value of the oil was added to the oil. The mixtures were then shaken slowly at 40° (when NaOH is used) or 50° (when Na_2CO_3 is used) and separated into 3 layers, soap, emulsion, and oil, by centrifuging. The latter two layers were washed with hot water several times and clear oils were obtained. The greater the acid values, the more difficult the separation of emulsion. Oils prepared by the extraction method are easier to handle than those prepared by press machines. Na_2CO_3 is recommended over NaOH. The color was better than when treated with acid alone. (*Chem. Abs.* **45**, 4064)

Studies of tung oil. I. Fatty acid. C. Chin (Formosan Univ. Formosa). *J. Chem. Soc. Japan,* Ind. Chem. Sect., 52, 215-16 (1949). The constitution of fatty acids of Formosan tung oil is: lauric acid 0.2, myristic 0.5, palmitic 3.0, stearic 2.2, oleic 15.8, and eleostearic 70.0%. It was found that α-eleostearic acid does not isomerize to the β-form by the ester interchange reaction, but does by distillation. (*Chem. Abs.* **45**, 4063)

PATENTS

Oil extraction process. J. W. Dunning (V. D. Anderson Co.). *U. S. 2,551,254.* High oil content seeds are mechanically expressed to reduce the oil content to about one-fourth of the total protein content. This material is then cracked, flaked and solvent extracted.

Process for refining cottonseed oil. W. Lange (Procter and Gamble Co.). *U. S. 2,551,496.* Crude cottonseed oil is mixed with salicyclic acid prior to neutralizing the free fatty acids with sodium hydroxide.

Process for treatment of gossypol in solvent-extracted cottonseed meal. M. Bonotto. *U. S. 2,551,581.* A process is described for treatment of solvent extracted cottonseed meal to reduce the gossypol content to safe feeding proportions which consists of adding ammonium carbonate (about 0.001%) to the solvent extracted meal, heating and then steaming this mixture.

Extraction column. G. V. Woody and C. W. Bilbe (Allis-Chalmers Mfg. Co.). *U. S. 2,551,820.* A method of introducing feed to the top of a liquid filled counter-current extraction column which is designed to reduce turbulence at the top of the column so permitting withdrawal of miscella of lowered fines content.

Solvent fractionation of fatty materials. F. E. Lacey and W. M. Leaders (Swift & Co.). *U. S. 2,552,797.* A process is described in which fatty material is decolorized in propane. A concentrated solution of the decolorized material in propane is then cooled to below 100°F. to precipitate the higher melting point constituents.

Solvent treatment. H. H. Young and H. C. Black (Swift & Co.). *U. S. 2,553,288.* A hydrogenated fat containing a substantial portion of mono and diglycerides is freed of flavor and odor by dissolving in a polar solvent, chilling the solution until two phases are formed, and removing the phase containing the materials which tend to cause reversion of flavor and odor.

Oxidation process to form free fatty acids. E. V. Fasce (Standard Oil Dev. Co.). *U. S. 2,553,364.* A mixture of olefines, alcohols and aldehydes formed from a synthesis reaction is washed with a dilute mineral acid solution, then washed free of acid and oxidized in the liquid phase with air in the presence of cobalt oleate to form fatty acids. The reaction temperature may vary from 0°-200° and the reaction time from 1-7 hours.

Decolorization of oils. R. Samuel. *French 948,401.* Oil is mixed with surface adsorbent catalysts, such as active charcoal, while submitting the mixture to a high-frequency agitation, e.g. ultrasonics of 400 kc./sec. at 700 watts output. (*Chem. Abs.* **45**, 4067)

Edible oil from fruit kernels. Badische Anilin- & Soda-Fabrik H. Schlecht and L. Schlecht). *German 801,645.* The stability and storage property of fruit kernels is improved by drying the latter to a water content of 5-10%, after washing with an aqueous NaCl solution or water. Freshly pressed grape seeds are washed with running water and thereafter dried with a hot-air current at 105°. The above treated grape seeds give, after 5 months' storage, on disintegration, extraction with benzene, and removal of the benzene by distillation, an edible oil of an acid no. of 0.3. Grape seeds which are not prewashed and predried yield on similar storage an edible oil of an acid no. of 18. (*Chem. Abs.* **45**, 3621)

• Biology and Nutrition

R. A. Reiners, Abstractor

The lipids contained in kidney, testes, and liver. E. Marchetti (Inst. Serono, Rome). *Rass. clin. terap. e sci. affini* **48**, 1-6 (1949). Extraction procedures and the resulting data are given for the determination of the cholesterol, lecithin, cephalin, cerebroside, and fatty acid content of bovine liver, kidney, and testes. (*Chem. Abs.* **45**, 3924)

Influence of the cow's feed on some constants of butter. P. Brozzetti (Univ. Perugia, Italy). *Mondo del latte,* Dec., **1947**, 11-15. Cows fed with (1) hay and wheat bran, (2) hay and tobacco-seed cake, (3) hay and linseed cake, (4) hay and almond cake, (5) hay and sunflower-seed cake, and (6) meal of extracted tobacco seeds, gave milk from which butter was obtained with the following average respective values for d., % fat, n^{40}, iodine no., Reichert-Meissl no., Polenske no. and Köttstorfer no.: 1.03, 3, 46, 40, 26, 2, 204. (*Chem. Abs.* **45**, 3952)

Fat synthesis by microorganisms and its possible applications in industry. H. Lundin (Roy. Inst. Technol., Stockholm). *J. Inst. Brewing* **56**, 17-28(1950). A review with 26 references. (*Chem. Abs.* **45**, 4061)

Identification of the volatile fatty acid in the peripheral blood and rumen of cattle and the blood of other species. G. L. McClymont (Vet. Research Sta., Glenfield). *Australian J. Agr. Research* **2**, 92-193(1951). Volatile fatty acids isolated from 9 samples of peripheral blood from 4 cows contained, on a molecular basis, 93% acetic acid, 2.4 propionic acid, 2.5 butyric acid, and 1.8 of a group of at least 3 acids between butyric and octanoic. Only traces of esterified acids lower than octanoic were found in bovine blood lipids. Volatile fatty acids, containing high proportions of acetic acid, were also found in the blood of the rabbit, guinea pig, horse, and pig, and in human plasma. (*Chem. Abs.* **45**, 3483)

Stratification of butter melt in ghee making. B. Badahur, M. R. Srinivasan and S. C. Ray (Indian Dairy Research Inst., Bangalore). *Indian J. Dairy Sci.* **3**, 94-106(1950). Clarification of butter to form ghee is accomplished by heating to form 3 layers, the middle one being liquid fat. By removing the bottom layer of buttermilk and heating the 2 top layers to 120°, the ghee contains less moisture and acid, and more vitamin A, and has a better aroma. (*Chem. Abs.* **45**, 3521)

Effects of a high-fat diet on the joints of aging mice. M. Silberberg and Ruth Silberberg (Hosp. Div., City of St. Louis, Mo.). *Arch. Path.* **50**, 828-46(1950). Male mice fed a diet containing 29% fat showed increased incidence and accelerated onset of osteoarthritis over the controls fed 5% fat. Overweight was not a significant factor in the occurrence of degenerative joint disease. (*Chem. Abs.* **45**, 3466)

Utilization of fatty acids in the liver and muscles of fasting animals. K. Ara (Keio Univ., Tokyo). *J. Biochem.* (Japan) **63**, 1-16(1944). Rats were on a standard diet to which 10% of either coconut oil, olive oil, or linseed oil was added. In the olive oil series the fat fatty acids (1.11%) and phosphatide fatty acids (2.05%) of the liver had an average iodine no. of 87.9 and 142.9, respectively, and of the muscles, 84.7 and 145.3, respectively. On coconut oil, the iodine values were 133.4 and 154.5 for the liver, and 107.6 and 155.3 for the muscles, respectively. And on linseed oil the iodine values were 82.0 and 158.6 for liver and 64.6 and 155.6 for muscles, respectively. As a result of 3-5 days' fastings the total liver fat fatty acid content decreases to about one-half and that of the muscles to about one-sixth; the phosphatide fatty acid content of the liver decreases to about one-half and that of the muscles to two-thirds. During fasting the iodine no. of fat fatty acids of liver and muscles generally increases (only in rats on a linseed-oil diet was there actually a decrease in liver) whereas the iodine no. of phosphatide fatty acids always showed a sharp decrease. (*Chem. Abs.* **45**, 3473)

The content in tissues of different unsaturated fat acids in neutral fat and in phosphatide on ordinary or on fat diets. K. Matsubara (Keio Univ., Tokyo). *J. Biochem.* (Japan) **36**, 17-41(1944). Pigeons on a diet containing linseed oil showed a great increase in the linoleic and linolenic acids of both muscle and liver fat, and the increase is much greater than in the phosphatide fraction. In pigeons on the coconut-oil diet there is a greater amount of oleic acid in liver fat as well as in the liver and muscle phosphatide than in pigeons on the regular stock diet; this suggests that the saturated acids must be transformed into unsaturated acids. (*Chem. Abs.* **45**, 3474)

Products of autoxidation of vitamin A. G. V. Troitskii (Veneral Inst., Moscow). *Biokhimiya* **15**, 485-9(1950). Various oxidation products of vitamin A exist in the blood and organs of animals and man. The epoxide is formed on exposing vitamin A to the air for 20-40 days. Further exposure results in the formation of a substance which gives a red color with $SbCl_3$. Finally, on prolonged exposure to the air, vitamin A is transformed into a substance which yields with $SbCl_3$ a color having an absorption spectrum at 420 mμ. (*Chem. Abs.* **45**, 3478)

The fate of branched-chain fat acids in animal body. III. Relation between optical activity and chemical change in vivo of aliphatic substances with branched chain. S. Akiya and T. Yamakawa (Univ., Tokyo). *J. Pharm Soc. Japan* **70**, 477-80 (1950). 2-Methylcaprylic acid, 3-methylpelargonic acid, 2-ethylcapronic acid, 2-ethylhexanol, 3-ethylenanthic acid, dibutylacetic acid, and dipropylpropionic acid were given to rabbits. In all cases, except 2-ethylhexanol which was recovered as carboxylic acid, they were excreted in urine as monocarboxylic acids without change and dicarboxylic acids excreted after ω-oxidation. In either case, $[\alpha]_D$ showed dextro rotation, though the values were not large. No evidence was obtained as to the assumption that biological oxidation, especially ω-oxidation, is asymmetric. (*Chem. Abs.* 45, 3479)

The fate of branched-chain fatty acids in the animal body. I. A contribution to the problem of Hildebrandt acid. M. Asano and T. Yamakawa. *J. Biochem.* (Japan) 37, 321-27(1950); *J. Pharm. Soc. Japan* 68, 147-9(1948). Rabbits fed l-rhodinic acid excreated a mixture of Hildebrandt acid and dihydro-Hildebrandt acid. (*Chem. Abs.* 45, 3478)

Vitamin A in milk. II. Vitamin A, carotene, and general composition of prepartum milkfat. T. M. Paul, M. G. Kalyanakrishnan, A. J. Lazarus, C. P. Anantakrishnan and K. C. Sen (Indian Dairy Research Inst., Bangalore). *Indian J. Dairy Sci.* 3, 112-26(1950). Milk collected from cows 15 days before parturition contained very high amounts of vitamin A and carotene. A gradual decrease until the day before parturition was followed by an increase then a second decrease to steady concentrations 5 days after parturition. Reichert values of the fat increased to parturition and became steady 5 days after parturition, whereas iodine values decreased. (*Chem. Abs.* 45, 3521)

Relation between tocopherol and carotene content of milk and its resistance to oxidized flavors. Anon. *Nutrition Rev.* 9, 118(1951). As the tocopherol content of milk fat is increased, the resistance of the milk to development of oxidized flavors is increased. There is a correlation between the tocopherol and carotenoid content of milk fat but no correlation between tocopherol and vitamin A content.

• Waxes

E. H. McMullen, Abstractor

Fatty alcohols from wool wax unsaponifiables by urea-complex formation. E. von Rudloff (Nat'l Chemical Research Lab., Council for Sci. and Ind. Research, Pretoria, South Africa). *Chem. and Ind.* 17, 338(1950). The fatty alcohols present in wool wax unsaponifiables were separated from components having more complex cyclic structures by formation of urea-complexes in ethanol. The complex is separated by filtration, purified by recrystallization from ethanol and decomposed in a mixture of water and ether. Analysis of the recrystallized mixture of monohydric alcohols indicates an average chain length of C_{26}. Further work is underway to separate and identify the individual alcohols.

The effect of coal preparation on yield of raw montan wax. H. Thieberger and V. Vcelák (Coal Research Inst., Prague, Czech.). *Paliva* 33, 262-9(1950). The pretreatment of coal has a marked effect on the yield of raw montan wax by extraction with organic solvents such as C_6H_6. The most convenient grain size for extraction is between 8 and 10 millimeters, depending on the coal type. The H_2O content should be between 10 and 18%. Thermal pretreatment of the coal at 250°, under pressure, may nearly double the yield of wax. Chemical pretreatment, such as by acid or base, effects a change in composition as shown by a higher pour point and different physical and chemical properties. Submitting coal to an electric current increases the yield of wax as is indicated by preliminary work. (*Chem. Abs.* 45, 4425)

Textile applications of synthetic waxes. J. H. Dollinger. *Rayon synth. Text.*, 31, 5, 106-107(1950). Synthetic waxes are relatively new industrial materials and their use in the textile industry as water repellents, delustrants, lubricants, etc., is still small but growing. They will probably never replace the low-cost paraffin waxes where these are already shown to be satisfactory textile processing aids. However, their unique properties, uniformity, and cheapness (compared with natural waxes) will cause intensive investigation which may expand their application. (*Brit. Abs.* BII, Oct., 1950, 955)

The lubrication of cotton and other textiles. E. Moss (Brit. Cotton Ind. Research Assoc., Manchester, England). *Brit. J. Applied Phys.*, Suppl. 1, 19-23(1951). A textile finishing process such as scouring with alkali, bleaching, dyeing, etc., removes the natural wax and may introduce other surface layers, all of which increase friction. Data are presented to show the reduction in friction by adding various lubricants including paraffin wax, tallow, mineral oil, octadecyl alcohol, fatty acids, and their esters and soaps. Chemical constitution of the lubricant has an effect on its lubricating power and also on the distribution of the lubricant on or in the fiber. Some undesirable side effects of lubrication that may occur are reduction in wettability, absorbency, and strength of the fiber. The effects of lubrication on regenerated celluloses such as viscose are broadly similar. (*Chem. Abs.* 45, 4458)

PATENTS

Refining of vegetable wax powder. A. F. Buckman, Jr. (S. C. Johnson & Son, Inc.). *U. S. 2,540,978.* Such impurities as leafy matter are separated from crude unmelted vegetable wax powder by agitating it with at least 250 weight % of H_2O and 0.25 weight % of water-soluble lignin or lignin sulfonate below 70°, letting it stand 90 minutes or more and recovering the wax layer from the surface. (*Chem. Abs.* 45, 4470)

Stable fluid wax emulsions. R. B. Porter, Jr., and E. J. Campbell (American Cyanamid Co.). *U. S. 2,541,006.* An emulsifier for vegetable and mineral waxes contains 50-80% oil-soluble, H_2O-dispersible alkali metal petroleum sulfonate, 0-25% fatty acid, such as oleic or stearic, 15-40% vegetable wax, such as carnauba or candelilla. One part emulsifier and six parts wax form a stable emulsion with seven parts H_2O. (*Chem. Abs.* 45, 4470)

Microcrystalline wax as an antifoam agent in soluble oil-water emulsion. E. H. Sperry (Sun Oil Co.). *U. S. 2,545,677.* The addition of microcrystalline wax to soluble oil compounds improves the resistance to foaming and imparts rapid defoaming properties. The most important properties of this wax are: flash point over 400°F., melting point 145-200°F., viscosity 50-105 sec./210°F., penetration (ASTM) 1-150, molecular weight 500-850. Briefly, the process comprises adding to a major portion of mineral oil, minor portions of a soap of petroleum naphthenic acid and wax. (*Chem. Abs.* 45, 4442)

• Drying Oils

Stuart A. Harrison, Abstractor

Fused copals and copal esters in the manufacture of preserve-can varnishes. L. J. Lees. *Ind. vernice* (Milan) 4, 232(1950). A pasteurizable varnish was prepared by heating 100 Kg. of a copal ester (m. 40-41°) and 125 Kg. of a 30 poise stand oil (25/75 wood oil/linseed oil) at 285° until compatible, adding another 125 Kg. of the oil and heating for another 20 minutes at 285° or until fully compatible. The varnish was cooled to 150° and 2.5 Kg. Co. (6%) linoleate were added, and 180 Kg. of white spirits were added to reduce the viscosity to 2.5 poises (25°). The varnish had an acid value of 4.5 and was applied by baking two hours at 110-125°. Varnishes can be made with fused copals or with pentaerythritol esters in place of glycerol esters by appropriate modification. The varnishes are for roller coating and are baked for 3-6 hours at 60°. (*Chem. Abs.* 45, 4059)

Stability of eleostearic acid during storage. R. W. Planck, F. C. Pack, and D. C. Heinzelman. *Proc. Am. Tung Oil Assoc.* 1950, 37. Samples of freshly prepared α- and β-eleostearic acids were stored under varying conditions of temperature, light, air, and solvents. The amounts of unchanged eleostearic acid were determined by spectrophotometric examination. Exposure of the dry crystals to the air at 4-35° resulted in conversion to viscous liquids only partially soluble in cyclohexane. The higher the temperature the more rapid was the conversion. The β isomer was relatively stable at 4°; the α acid was stable at —40°. The influence of light was negligible. Samples of the acids stored in evacuated ampules at —40° to 35° were stable. When made into pastes with ethyl alcohol and stored in completely filled containers, β-eleostearic was stable up to 35°. (*Chem. Abs.* 45, 3611)

Some aspects of the oxidation of the drying oils. L. Williamson. *J. Oil & Colour Chemists' Assoc.* 34, No. 369, 119(1951). Oxidative polymerization plays an important role in the gelation and drying of oils and oil modified resins. Studies of the oxidation of the simple methyl esters of the unsaturated fatty acids has revealed much about the mechanism of this process.

Entry of oxygen into the drying oil takes place through the activation of the α-methylene group by light as catalyst. This is a slow process with a mono-olefin such as methyl oleate but at room temperature or slightly higher (35°) measurable amounts of methyl oleate hydro-peroxide are formed. Thermal decomposition of this hydroperoxide in an enert atmosphere gives in addition to other products an oxygen bonded dimer, which still has two double bonds per mol. The hydroperoxide formation is largely the result of a chain reaction involving the removal of the α-methylenic hydrogen by a peroxide radical (ROO·). The radical so formed adds oxygen to form a new peroxide radical. Methyl linoleate reacts more rapidly but in a manner analogous to methyl oleate on activated oxidation. The thermal decomposition of the peroxidized methyl linoleate differs in the respect that the dimers are carbon to carbon linked instead of oxygen linked. These dimers have one pair of conjugated double bonds per mol plus one or two unconjugated double bonds. The influence of such metal catalysts as cobalt, lead, manganese, and copper salts is discussed. They are thought to act as oxygen carriers and a free radical mechanism is advanced to account for the observed reaction velocities. Though it is recognized that the polyester formation in drying oils complicates the picture, it is believed that the same reaction mechanisms are in operation here as in the case of the simple esters.

The influence of ozone on paint vehicles and some other macromolecular products. F. J. Hermann, H. W. Talen, and G. J. Scheffer. *Centraal Inst. Materiaal Onderzoek Afdel. Verf, Circ.* No. 68(1950). Films of stand oil-phenolic varnish, tung oil-phenolic varnish, alkyd varnish, nitro cellulose containing maleic resin, castor oil and dibutyl phthalate, rubber, neoprene, hydrochlorinated rubber, polyethylene and polyvinyl chloride-acetate were stretched and exposed to ozone. Rubber, neoprene, and hydrochlorinated rubber cracked; the others did not. The stand oil-varnish and tung oil-phenolic varnish increased in tensile. Ozone caused cracks only in those stretched samples which possessed elastic properties and unsaturated carbon to carbon double bonds. (*Chem. Abs.* **45**, 3610)

Properties of alkylphenolic resin varnishes. R. Dooper and F. J. Hermann. *Centraal inst. Materiaal Onderzoek Afdel. Verf, Circ.* No. 67(1950). Varnishes were prepared from 1 part of alkali-catalyzed phenolic resins and two parts of the following oils: tung, linseed and blown linseed. The tung oil reacted most rapidly on cooking followed by blown linseed oil. The varnishes made with tung were lightest and linseed darkest. The tung oil varnishes dried the quickest, followed by linseed. The linseed and blown linseed varnishes had slightly better water resistance. In exterior exposure the blown linseed varnish had somewhat better gloss retention than the other two. (*Chem. Abs.* **45**, 3611)

Drying oils—past, present and future. W. G. Andrews. *Paint Oil Chem. Rev.* **114**, No. 8, 10(1951). A study of the use of drying oils during the past twenty years is given. The use of tung oil has been relatively stable except for a short period during the war when it was nearly impossible to obtain from China. The use of castor oil, perilla and oiticica has steadily declined during this period. Except for the year 1949 more linseed oil is used each year in drying oil products than all other oils combined. The second most widely used drying oil during the past eight years is soybean oil. It has steadily increased since 1930. During the past three years no linseed oil has been imported. It appears that in the immediate future we must depend on domestic drying oils for use in protective coatings.

An accelerated storage test for paints. N. B. Garlock. *Official Digest Federation Paint & Varnish Production Clubs* No. 316, 306(1951). A study of the tendency of some paints to develop hard settled cakes while others did not, led to the discovery that temperature extremes promote hard settling. An accelerated testing procedure was developed which involved subjecting samples of paint to cycles of high and low temperatures. Fifteen cycles of eight days at 140°F. and four days at −10°F. gave results showing good correlation with 18 months of normal storage.

Film forming materials investigation. On catalytic solidification. M. Kronstein. *Paint Varnish Production* **41**, No. 5, 17 (1951). Tung oil was treated with various concentrations of anhydrous ferric chloride dissolved in tricresyl phosphate. At room temperature the gelation time decreased rapidly with increased concentration of ferric chloride. Increased temperature also decreased the gelation time, at 50° gelation occurred in 5-6 minutes while it occurred in 200 minutes at room temperature. Ferric chloride does not enter the gel. Other drying oils which are brought near the gelation point by heating are not affected by ferric chloride. Other metallic halides have a similar effect on tung oil. When heat gelled tung oil is exposed to allyl mercaptan or diallyl sulfide reaction occurs and sulfur is found in the product. A similar treatment with different trichlorosilanes showed that combination occurred to yield silicon-containing products.

Alkali attack on paint. G. W. Mack. *Paint Manuf.* **21**, No. 4, 121(1951). A study was made of the mechanism of alkaline attack of paint films on alkaline materials such as cement, asbestos cement, plasters, and other surfaces containing lime. Conclusions from study were that the alkali attack is caused by alkali metal hydroxides. The presence of moisture contributes heavily to the attack. Pretreatments of surface with inorganic salts affords some margin of safety. Impermeable alkali-resistant primers can be successful but may fail in other ways if conditions are damp.

Accelerated weathering of paint and varnish films. P. J. Gay, *J. Oil & Colour Chemists' Assoc.* **34**, No. 368, 43(1951). A comprehensive study of the factors of "weather" which lead to break down of a paint film was made. Apparatus which was designed for accelerated weathering tests is described. Using this apparatus the intensity and time of ultraviolet irradiation, amount of water treatment, period of revolution of test drum and oxygen pressure were varied. A large number of vehicles and pigments were studied under a variety of conditions. The results of the study indicate that the simple water spray-arc lamp cycle accelerated weathering machine does not duplicate the type of breakdown obtained on out-door exposure. This results because the chemical aging of the entire film does not keep pace with the surface aging. Indications are that a more realistic accelerated aging can be achieved by increasing the oxygen pressure during the weathering cycle.

PATENTS

Modified alkyd resins and coating compositions containing the same admixture with readily copolymerizable vinyl monomers. H. E. Adams. *U. S. 2,537,949.* Rosin (4.0 mols) and maleic anhydride (6.0 mols) are heated for three hours at 200° in an inert atmosphere. The rosin and maleic anhydride condense to form a tribasic acid. To this product is added linseed oil fatty acids (2.0 mols), diethylene glycol (6.4 mols), glycerine (2.2 mols) and the mixture refluxed at 225° for 5½ hours. The acid number at this time is 70 and heating is discontinued to prevent gelation. The product is cooled by adding xylene. At 120° methyl alcohol is added to give an 80-20 xylene-methanol solution with 75% solids. A master batch is made by mixing 400 g. of the above resin vehicle on a paint mill with 300 g. of pigment such as ferrite yellow, magnesium silicate etc. To the master batch (264 pts.) are added 6% cobalt dried (3 pts.), styrene (180 pts.) and 80-20 xylene-methylalcohol (50 pts.). This composition has good coating characteristics and dries very rapidly. An air-dried sample dried to "dry to touch" in 2 minutes.

Process for improving the drying qualities of tall oil. W. C. Spitzer. *U. S. 2,539,975.* Tall oil acids are air blown at 270° and then glycerine and a PbO catalyst are added. Esterification is carried out at 180° for one hour and then finished at 285° for 5 hours. The set time and tack free time of drawn films are reduced by more than one-half over similar polyesters prepared without blowing. Other polyhydric alcohols may be used in place of glycerine.

Wrinkle finishes. E. W. Moffett. *U. S. 2,548,388.* A product is prepared, which will give a wrinkle finish when properly applied and baked, by heating the following materials to 350°-425°F. for 16-20 hours: 1 mole carbic anhydride (Diels-Alder addition product of maleic anhydride and cyclopentadiene), 0.1-0.4 mole of drying oil monoglycerides and enough diethylene glycol to provide a 10-25% excess of hydroxyls over carboxyls in the mixture. Such drying oils as linseed, oiticica, dehydrated castor and tung may be used. Other glycols will also serve in place of diethylene glycol.

Stand oils. W. Schlick. *German 801,644.* In the manufacture of stand oils from linseed oil, sometimes in admixture with 10-20% of other drying oils such as wood oil, oiticica oil, or soybean oil, the boiling time may be reduced by heating in a closed vessel at 280-300° while constantly blowing a cold air current over the oil surface and sucking off air and oil vapors until the oil consistancy has reached the desired stage. The absorbed oxygen saturates the double bonds of the contained linolenates and promotes cyclization of the oil molecules which accelerates the polymerization process. (*Chem. Abs.* **45**, 3614)

• Detergents

Lenore Petchaft, Abstractor

Fatty acids for soap manufacture. P. I. Smith. *Am. Perfumer Essent. Oil Rev.* 57, 131-2(1951). Advantages and economics of soap made with fat acids and with glycerides are discussed. (*Chem. Abs.* 45, 4063)

Polysoaps. I. Viscosity and solubilization studies on an n-dodecyl bromide addition compound of poly-2-vinylpyridine. U. P. Strauss and E. G. Jackson (Rutgers U., New Brunswick, New Jersey). *J. Polymer Sci.* 6, 649-59(1951). Polysoaps are defined as polymers to whose chain soap molecules are attached. Through the reaction of poly-2-vinylpyridine with n-dodecyl bromide such a polysoap was prepared in which 33.7% of the nitrogens were quaternized. This polysoap exhibited reduced viscosities in aqueous solution which were smaller than those of the parent polymer and of the polysoap in ethanol. The relatively compact structure of the polysoap molecule in water, which this indicates, is thought to be caused by micelle formation of the soap molecules attached to the polymer chain. This idea is substantiated by the fact that the polysoap acts as a solubilizer for isooctane in water.

Carboxymethylcellulose in laundries. R. Smit and R. J. Nieuwenhuis. *Witwasserij-Ind.* 5, No. 3, 9-13(1948). Practical tests of the use of CMC in laundering white and patterned materials are reported. Improvement in the tint of white material, and brightening of the colors of patterned material were due to the fact that dirt remains in suspension. (*Chem. Abs.* 45, 4066)

Toilet bar from synthetics. V. J. Keenan (Atlantic Refining Co., Philadelphia, Pa.). *Soap Sanit. Chemicals* 27, No. 5, 27-30, 82, 135(1951). An all-synthetic detergent milled toilet bar has been developed from a formula based on "Ultrawet" alkylaryl sulfonate. The finished product contains about 50% detergent together with soya lecithin as a detackifier, corn starch for hardening properties and talc to provide slush resistance. The compounded bar stock can be processed in conventional soap plodders and presses to yield a hard smooth well-formed bar which foams and deterges effectively in the hardest water. On the skin, the composition is free rinsing and it leaves no residual "tack." The bar dries out with satisfactory rapidity and compares with soap bars in durability and number of washings. It enjoys the further advantages of being non-alkaline, thus furnishing an alternative to soap for users with sensitive skins.

The function of dyeing assistants. R. A. Lindermaier. *Textile Age* 15, No. 1, 30-1, 32, 33, 34-5(1951). Two dye-leveling agents, one sulfated with emphasis on wetting action and the other an acid amide with emphasis on lubricating and detergent properties, are discussed as representative dye assistants. (*Chem. Abs.* 45, 2209)

How to use silicates in soap. P. I. Smith. *Am. Perfumer Essent. Oil Rev.* 57, 305-6(1951). The main advantages of adding silicates to soap are as follows: they give pH values higher than those of other alkaline salts at the same concentration, they exercise a valuable buffering action on detergent solutions and help maintain constant pH, they exercise a pronounced wetting-out action and are helpful in laundry soap, they inhibit deterioration of certain soaps due to rancidity changes, they build a quick and lasting suds with soap, have powerful peptizing and deflocculation action, and inhibit corrosive action of the detergent on metals. The range of silicate properties from viscous to crystalline, depending on silica ratio, results in many applications of these compounds for many types of soap products.

The effect of salts on the critical concentration, size, and stability of soap micelles. M. E. Hobbs (Duke University, Durham, North Carolina). *J. Phys. Colloid Chem.* 55, 675-83(1951). A theory is presented which explains, along the general lines of Debye's theory of the soap micelle, the essential features of the behavior of soap molecules in dilute salt solutions. The fact that soap micelles increase in size upon addition of salt is related to the ionic strength of the solution for the limited case of micelle surfaces of low charge density. This theory also predicts unlimited size of the micelle at a predetermined ionic strength. Three important features of the soap micelle system are (1) the magnitude of the critical concentration C_0, (2) the change of C_0 with added salt, and (3) the fact that only the gegen ion is of importance in determining the behavior of the micelle. These three factors are semiquantitatively accounted for by a theory that was modified to include the case of a micelle and surface of high charge density.

Cosolubilization in solutions of potassium laurate. The effect of cosolubilized alcohols and hydrocarbons on the solubilization of several aromatic compounds in potassium laurate solutions. I. M. Kolthoff and W. F. Graydon (University of Minnesota, Minneapolis, Minn.). *J. Phys. Colloid Chem.* 55, 699-712(1951). The effect of cosolubilized amyl alcohol, octyl alcohol, pentane, octane, and diisoamyl on the solubilization by potassium laurate of dimethylaminoazobenzene, Orange OT, and trans-azobenzene has been measured at 30°. The effect of cosolubilized octyl alcohol on the solubilization of m-dinitrobenzene, α-naphthol, and naphthalene has also been determined.

Determination of detergency with artificially soiled fabric. G. Reutenauer and Mme. S. Dupin (Lab. Chevreul, Paris). *Bull. mens. ITERG.* 5, 84-90(1951). Artificial soils of carbon black prepared with the use of oils containing unsaturated fatty acids cannot be removed even by repeated washing. The use of hydrogenated oils makes it rather difficult to obtain a uniform distribution of the soil. Soak cotton fabric (5 m. × 26 cm.) 30 minutes at 40° in a solution of 0.7% "Rapidase" to eliminate the dressing, rinse, dry, iron, immerse for 2 minutes in a mixture of 500 ml. mineral oil SAE 40, 125 g. coconut oil, 2 g. anthracene gas black, and 300 ml. white spirit at 110-190°, and pass twice through a wringer. Wash several times in countercurrent, first with white spirit that has been used in a previous operation, then with pure white spirit, and dry. In washing tests in a launderometer with fabric soiled as described and with soils procured from the official Swiss Laboratory the following respective differences of reflectance before and after washing were obtained with various detergents: sulfonated oleic alcohol 17.8, 26.5; hard soap 17.6, 24.5; mixture containing 20% alkylarylsulfonate, phosphate, and carboxymethylcellulose 14.7, 21.5; secondary alkyl sulfate (20%) 14.5, 19.5; Na salt of oleylmethyltauride (30%) 14.0, 19.0; Na oleate 13.5, 18.5; Na alkylsulfonate (40%) 12.0, 16.5; sulfonate hydroxyethylamide of palm-kernel-oil acids (95%) 6.5, 12; K laurate 7.0, 11.5; Na carbonate 5.0, 8.5; water 4.0, 5.50. (*Chem. Abs.* 45, 4066)

PATENTS

Detergent composition. D. W. Jayne, Jr. (American Cyanamid Co.). *U. S. 2,545,357.* A detergent composition comprising the sodium salt of an ester of phosphoric acid and an amide obtained by condensation of a fatty acid having from six to eighteen carbon atoms with a member of the group consisting of primary- and secondary-amine alcohols in a 1:1 molar ratio, trisodium phosphate and a sufficient amount of soda ash to produce a dry, free-flowing powder.

Sulfonic acid surface active agent and method of preparation. G. W. Hedrick (E. F. Houghton and Co.). *U. S. 2,548,017.* An improved wetting agent consisting of the water-soluble salts of benzoyl sulphopropionic acid esters.

Noncorrosive detergent composition. J. C. Harris (Monsanto Chemical Co.). *U. S. 2,550,691.* Preparation of a noncorrosive detergent for use in automatic washing machines made of aluminum or vitreous enameled metal, consisting of the condensation product of tall oil-ethylene oxide in combination with tetrasodium pyrophosphate, sodium silicate, starch, sodium carbonate and carboxymethylcellulose.

Process of sulfating alkylolamides to form detergents. R. A. Henry (Procter & Gamble Co.). *U. S. 2,551,125.* Process of sulfating an alkylolamide to form wetting, foaming and detergent agents in which the alkylolamide (myristic ethanolamide) is added with vigorous stirring to chlorosulfonic acid followed by neutralization with sodium hydroxide.

Improved soapless detergents. F. J. Pollak (Imperial Chemical Industries, Ltd.). *British 650,222.* A process for the production of stable and aqueous compositions of higher viscosity than anionic surface-active soapless detergents alone, in which the new composition is prepared by admixing water, an anionic surface-active soapless detergent and a water-soluble alkali metal salt of a carboxymethylcellulose so that the soapless detergent is in a quantity of not more than 8% and that of the carboxymethylcellulose of not less than 2% present in the composition.

Continuous soap making. E. Schueller, A. Beck, and F. L. Lachampt. *French 946,746.* Tallow or like fat at 45° is mixed and homogenized with 1-2% above the theoretical amount of 40% NaOH, to give a water-in-oil emulsion, the amounts being measured automatically. The temperature is increased to 100° and, when the saponification is complete, the mixture is washed twice with a 12% NaOH solution, the small amount of alkali left then being neutralized with a free fatty acid or triethanolamine sulforicinoleate. Automatic control of the saponification is achieved by use of a photoelectric cell to observe the clarity of the solution or the change in color of a pH indicator. (*Chem. Abs.* 45, 3622)