### **Oils and Fats**

RECOVERY AND PURIFICATION OF SEWAGE GREASE AT JOHANNESBURG. H. Wilson (Johannesburg, S. Africa). City Eng. Ann. Rept. 1945, 56-7. Process: Heating with crude  $H_2SO_4$ ; washing with hot water; heating with Twitchell reagent; washing with hot water; neutralization with ground limestone; distillation with steam from Cu still; casting of crude acids in slabs; pressing cooled acids to squeeze out liquid acids from crystalline fat acids; redistillation of liquid and repressing. From 1200 to 1400 lbs. of crude wet grease about 400-500 lbs. of mixed distilled fat acids could be obtained daily, yielding about 150 lbs. of "oleic" acid and 300 lbs. of "stearic" acid and 50-100 lbs. still-residue grease. Products made excellent shaving soaps and creams and other cosmetics. (Chem. Abs. 40, 6723.)

EMERSOL PROCESS. R. L. Demmerle (60 East 42nd St., New York, N. Y.). Ind. Eng. Chem. 39, 126-31 (1947). Equipment and method for fractionating 30-40 tons of fat acids per day are described. The acids are distilled to remove color, odor, neutral fat, and unsaponifiable material. Fat acids plus 1% crystals of one of the acids are proportioned countercurrently with 90% MeOH through control refrigerated crystallizing tubes. Motor driven scrapers prevent adherence of crystals to the walls. Crystals are removed from the slurry and washed with solvent by use of a rotary, vacuum filter situated in a refrigerated room. The solid cake, containing 30-60% solvent is distilled. The solvent-fat acid solution is treated with steam to remove some solvent and to add enough water to permit separation of the acids by decantation. The cost of the process is 65% less than that of the common mechanical pressing method for preparation of the stearic acid. The difference is due mainly to the high labor cost of the batch method. In the development of the new continuous process much relevant information was evolved. Petroleum ether and chlorinated hydrocarbon as solvent gave flat, pearly, plate type crystals which, because of their structure, had bad filtering characteristics; acetone, MeOH, and EtOH containing some water yielded the desirable granular needlelike crystals. Stability and ease of removal were the criteria for the choice made from among these.

THE EFFECT OF GAS DISCHARGES ON OILS AND FAT ACIDS. A. Nikuradse and A. Berger (Tech. Hoch-schule, Berlin). Physik. Z. 45, 71-81 (1944). The permanent physico-chemical changes resulting from discharges in H (8-10 Torr) were determined for rape oil, linseed oils, paraffin oil, oleic acid, and stearic acid in a special apparatus. The specific gravity and molecular weight increase with condensation. The increase in dielectric constant and polarization is proportional to the increase in viscosity, polar substances showing the greater change. The curvature of the viscocity-temperature curves is caused by the dependence of dipole fluids on temperature and by association, a convex curve meaning a decrease in size with increasing temperature. For similar polarization, field strength, and temperature, the log of the viscosity is proportional to the molecular weight. I numbers show that the hydrogenation of the unsatu-

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rated compounds is accompanied by the formation of new unsaturated compounds so that a state of equilibrium is reached.  $H_2O$  is formed from the fat acids probably by hydrogenation of the  $-CO_2H$  group to form -CHO or  $-CH_2OH$ . (*Chem. Abs. 40*, 6922.)

STUDY OF THE HEXABROMIDE NUMBER. J. P. Kass (Interchemical Corp., New York), W. R. Roy, and G. O. Burr. Anal. Chem. 19, 21-4 (1947). The problems involved in the determination of linolenic acid by the precipitation of its hexabromide are discussed. An adequate procedure gives consistent results and an analytical precipitate identical in appearance with pure hexabromostearic acid. The empirical nature of the hexabromide numbers is emphasized and the specification of experimental procedure is recommended.

THE EFFECT OF TISSUE FAT STABILITY ON DETERIORA-TION OF FROZEN POULTRY. M. L. Schreiber, G. E. Vail, R. M. Conrad, and L. F. Payne (Kansas Agr. Exper. Sta., Manhattan). *Poultry Sci. 26*, 14-19 (1947). It has been found that the oxidation-induction period of extracted fat does not give a reliable prediction of the stability of poultry fat *in situ* during frozen storage. Alfalfa or fish oil fed to chickens for 1 or 2 weeks before slaughter greatly decreases the stability of the fat of the carcass during frozen storage and hence also decreases the useful storage life of the poultry.

RANCIDITY DEVELOPMENT IN RAW VERSUS PRECOOKED FROZEN PORK SAUSAGE. B. M. Watts (State Coll. Washington) and Da-Hwei Peng. J. Home Econ. 39, 88-92 (1947). Rate of rancidification of raw ground pork in freezing storage increased rapidly with decreasing pH of the meat, within the pH range 6.5-4.8. The pH had no effect on rancidification of precooked ground pork. Except at the upper limits of the normal pH range of fresh pork, the precooked meat kept better than the raw. Certain salts (NaCl, NaNO<sub>3</sub>, NaC<sub>2</sub>H<sub>3</sub>O<sub>2</sub>, MgCl<sub>2</sub>, and KNO<sub>3</sub>) had a marked accelerating effect on rancidity development in raw ground pork in freezing storage but not on precooked ground pork. Other salts, KCl and Na<sub>2</sub>SO<sub>4</sub> had no effect. The effects of acids and salts on rancidity development in raw pork are believed to be due to the activity of a fat peroxidizing enzyme, possibly hemoglobin. Decomposition of the hemoglobin, with a resulting discoloration of the meat, accompanied rancidification.

STABILITY OF VITAMIN A IN SESAME OIL. S. Sen-Gupta (Bengal Immunity Res. Lab., Calcutta). J. Indian Chem. Soc. 23, 233-4 (1946). Vitamin A in vitaminized sesame oil is rapidly destroyed.

SEASONAL VARIATIONS IN THE VITAMIN A AND THE CAROTENE CONTENT OF RETAIL BUTTERS. H. A. Ellenberger, N. B. Guerrant, and O. B. Fardig (Pennsylvania State College, State College). J. Nutr. 33, 39-52 (1947). Although distinct seasonal variations in the carotene and vitamin A content of butters as purchased on the retail market in Pennsylvania were noted, there was no indication that any one brand of butter was constantly higher or constantly lower than other brands with respect to either vitamin A or carotene. A comparison of the seasonal vitamin A potencies of the commercial butters with those of the butter from the local creamery and with vitamin values reported in the literature for fresh butters indicated that during the course of this study the vitamin content of butter was relatively stable and that not much time elapsed from the date of manufacture until the butter reached the consumer.

THE AMINES OF HIGHER FATS. F. Bouquet. Inds. corp gras 2, 376-80 (1946). This comprehensive review treats general methods of preparation of amines from fats, chemical and catalytic amination of alcohols, chemical and catalytic reduction of amides, hydrogenation of nitriles, properties of amines, and their uses.

SIMPLE LABORATORY PREPARATION OF NITRILES AND AMINE DERIVATIVES OF FAT ACIDS. G. Reutenauer and C. Paquot (Lab. Chevreul). Inds. corps gras 2, 336-40 (1946). The apparatus and method for preparation of nitriles of Ralston et al. is simplified. A round bottom flask was surmounted with a 80 x 1.5 cm. tube containing in a small portion some beads in place of the Al<sub>2</sub>O<sub>3</sub> catalyst. The optimum amount of beads and necessary heat is to be determined by trials with each fat acid. The methods of manufacturing amines from the amides by reduction with Na and hydrogenation with common catalyst are reviewed. Methods using hydrogenation in neutral (A) and basic (B) solution are presented. The reaction apparatus is an electrical heated cylinder of 0.5 l. capacity and supplied with agitator. Method A: dissolve 30 g. stearonitrile in 100 cc. acetic anhydride, add 7 g. Raney Ni catalyst and hydrogenate 5 hours at room temperature. Method B: a solution containing 6 g.  $Na_2CO_3$ , 50 cc.  $H_2O$ , 50 cc. EtOH, and 30 g. stearonitrile is hydrogenated with the presence of 40% Raney Ni. Reduction is rapid. Only a small supplementary absorption is obtained on warming to 70°.

HIGHER FATTY ACID DERIVATIVES OF PROTEINS. W. G. Gordon (Eastern Regional Res. Labs., Philadelphia, Pa.), A. E. Brown, and R. W. Jackson. Ind. Eng. Chem. 38, 1239-42 (1946). The affinity of casein and a number of other industrial proteins for water may be reduced by acylation in aqueous alkali with higher fatty acid chlorides. Under otherwise identical conditions maximal acylation of casein is favored at the higher pH values investigated-namely, pH 10-12. Fatty acid chlorides ranging from C<sub>s</sub> to C<sub>1s</sub> in chain length yield essentially similar casein derivatives. The products, which may contain as much as 26%fatty acid radical, are obtained in amounts usually larger than the original weights of unmodified protein. Substitution occurs at the free amino and phenolic hydroxyl groups of the protein and probably at other reactive sites.

ISOLATION AND IDENTIFICATION OF FATTY ACIDS AS BIS-(*p*-DIMETHYLAMINOPHENYL)-UREIDES. F. L. Breusch and E. Ulusoy (Univ. Istanbul, Turkey). Arch. Biochem. 11, 489-98 (1946). The direct isolation of free fatty acids from fat mixtures takes place readily by the mere heating of their ethereal solution with bis-(*p*-dimethylaminophenyl)-urea. Crystalline fatty acid ureides precipitate. Properties, melting points, solubilities in ether, acetone, ethanol, and Et acetate, of the ureides of saturated fatty acids from C<sub>1</sub> to C<sub>20</sub>, of some unsaturated fatty acids and of  $\beta$ -hydroxy fatty acids are described. The introduction of this procedure in the analytical chemistry of fats is recommended.

NAPHTHALENE SERIES. X. THE PREPARATION AND THE PROPERTIES OF 1-STEAROYL-, 1-PALMITOYL- AND 1-

LAUROYL-2-NAPHTHOLS. R. D. Desai and W. S. Waravdekar (Univ. Bombay). Proc. Indian Acad. Sci. 23A, 341-6 (1946). Stearic acid, 2-naphthol, and anhydrous ZnCl<sub>2</sub> reacted to give 30% 1-stearoyl-2naphthol, m. 125-6°. (Chem. Abs. 40, 6455-6).

A COMPARISON OF THE NUTRITIVE VALUE OF FATS WHEN FED ALONE OR WHEN FED WITH SUCROSE OR LAC-TOSE. B. H. Ershoff and H. J. Deuel (Univ. So. Calif. School Med., Los Angeles). Am. J. Physiol. 148, 45-50 (1947). Male and female rats were fed diets containing 70% sugar (lactose or sucrose) and 30% fat. When lactose was the dietary carbohydrate, survival was significantly longer on rations containing margarine fat or butter fat than on diets containing corn oil or cottonseed oil. With sucrose as the dietary carbohydrate, no significant differences in length of survival were observed. Male and female rats were fed diets consisting of a single fat. With female rats of the U.S.C. strain, length of survival was longest with butter fat as compared with lard, olive oil, corn oil, margarine fat, soybean oil, wheat germ oil and cottonseed oil but the only significant difference was between the butter fat and cottonseed oil groups. With females of the Sprague-Dawley strain, results on butter were significantly better than with margarine fat, corn oil or cottonseed oil. No significant differences in length of survival were observed in male rats fed the above fats. Periods of survival of male rats on sugar-fat mixtures as well as on exclusive fat diets were longer than those of female rats. In a number of cases these differences were significant. There is some evidence of a strain difference in survival periods. Female rats of the U.S.C. strain lived longer on the vegetable fats than rats of the Sprague-Dawley strain.

REVIEW OF DISTURBANCES OF FAT ABSORPTION AND FAT DIGESTION. M. M. Kirschen and B. J. Weinberg (Michael Reese Hospital, Chicago, Ill.). Am. J. Digestive Diseases 14, 30-4 (1947). The causative factors accompanying abnormal fat excretion are classified into 3 main groups and each is discussed.

THE INFLUENCE OF THE RATE OF FAT DEPOSITION ON THE FIRMNESS OF THE FAT OF HOGS. W. L. Robison. Ohio Agr. Exper. Sta. Bull. 664, 26 pp. (1946). Refractive indexes of rendered samples of back fat, both when the samples were taken from the same hogs at weights of 100, 150, 200, and 250 pounds and when they were taken from hogs slaughtered at the different weights, showed that as hogs became heavier their fat became less soft or more firm. When they were fed the same ration and slaughtered at the same weight, the fat of rapid gaining hogs was slightly firmer or less soft than was the fat of hogs which had gained more slowly. The rations contained from 2.6-8.7% of fat. Both the rate of fat deposition and the weight or degree of fatness at slaughter influenced the firmness of the pork but not to as great an extent as did the fat content of the feed.

CHOLESTEROL AND FAT TRANSPORT. P. Favarger (Univ. Geneve, Switz.). Arch. intern. pharmacodynamie 72, 1-12 (1946). Normal human fasting serum esterifies cholesterol and 0.15 g./hr. of fat is transported by the serum in this state. During digestion more cholesterol is esterified and the serum transports about 1.0 g./hr. (Chem. Abs. 40, 7337-8.)

REMOVAL OF PLASMA PHOSPHOLIPIDES AS A FUNCTION OF THE LIVER: THE EFFECT OF EXCLUSION OF THE LIVER ON THE TURNOVER RATE OF PLASMA PHOSPHOLIPIDES AS MEASURED WITH RADIOACTIVE PHOSPHORUS. C. Entenman, I. L. Chaikoff, and D. B. Zilversmit (Univ. California Med. School, Berkeley). J. Biol. Chem. 166, 15-23 (1946). The concentration of phospholipides, total fatty acids, and cholesterol in plasma is not appreciably decreased by excluding the liver from the circulation. The rate at which intravenously injected radiophospholipide disappears from the plasma was used as a measure of the turnover time of plasma phospholipides. In confirmation of earlier work, it was found that plasma phospholipides are completely turned over in 6-10 hours in normal dogs weighing from 7-18 kg. By depriving these dogs of their livers, the time required for complete turnover was prolonged to 33-160 hours. It is concluded that the liver is the principal tissue in the body concerned not only with the synthesis and supply of plasma phospholipides but also with their removal.

SPECIFIC DYNAMIC ACTION OF DIETS HIGH IN CARBO-HYDRATE OR FAT. G. C. Ring (Ohio State Univ., Columbus). J. Nutr. 32, 653-8 (1946). The S.D.A. on a high carbohydrate diet  $(6.65 \pm 0.33\%)$  of energy in food ingested) is about the same as that of a high fat diet  $(7.10 \pm 0.60\%)$  containing same amount of protein. Respiratory metabolism for quiet periods during the 8 hours subsequent to the ingestion of a meal high in carbohydrate averaged 0.998 cal. per 100 g. per hour, and is almost the same as after ingesting an isocaloric meal high in fat—1.002 cal. per 100 g. per hour.

ESSENTIAL FATTY ACIDS AND HUMAN NUTRITION. A. E. Hansen (Univ. Texas School of Med., Galveston) and G. O. Burr. J. Am. Med. Assoc. 132, 855-9 (1946). In regard to clinical observations made thus far with human subjects, there is no evidence to indicate that a lack of the essential fatty acids produces a disturbance in growth, hematuria, kidney lesions, impaired reproduction, lactation or sterility, which abnormalities are attributed to the dietary lack of either linoleic or arachidonic acid in small experimental animals. However, as one of the most characteristic findings in all animal studies is an alteration in the appearance and character of the skin, it is perhaps not surprising to find a possible relationship between dietary fat and the skin in some human subjects.

INFLUENCE OF CHOLINE AND METHIONINE ON PHOS-PHOLIPIDE ACTIVITY AND TOTAL LIPIDE CONTENT OF LIVERS OF YOUNG WHITE RATS. M. G. Horning and H. C. Eckstein (Univ. Michigan, Ann Arbor). J. Biol. Chem. 166, 711-20 (1946). The oral administration of methionine or choline is usually followed by an increased transport of radioactive P to the phospholipide fraction of the liver as well as a slight increase in concentration of liver phospholipides. These increases are not always accompanied by a fall in liver lipide content and may not be related to lipotropic action. Under the conditions obtaining in these experiments it was not possible to detect elaidic acid in the phospholipides of the livers of young male rats that had ingested considerable amounts of elaidin.

THE EFFECTS OF INSULIN ON THE INCREASE IN LIVER FAT PRODUCED BY ANTERIOR PITUITARY EXTRACTS. J. Campbell (Univ. Toronto). Am. J. Physiol. 147, 742-7 (1946). In fasting rats, mice, and guinea pigs, the increase in liver fat which occurs in response to the administration of an anterior pituitary extract is partially inhibited by insulin. ACTIVITY OF ESTRONE AS A LIPOTROPIC FACTOR. P. György and C. S. Rose (Univ. Pennsylvania, Philadelphia) and R. A. Shipley. Arch. Biochem. 12, 125-33 (1946). Estrone shows a small but definite lipotropic effect when fed at a level of 30  $\gamma$ / day to intact and castrated female rats on a diet which produces fatty livers. When estrone is used with methionine it augments greatly the lipotropic action of the latter and essentially normal liver fat values are obtained. No explanation has yet been found for this action by estrone.

FATTY ACID METABOLISM. V. THE CONVERSION OF FATTY ACID INTERMEDIATES TO CITRATE, STUDIED WITH THE AID OF ISOTOPIC CARBON. S. Weinhouse, G. Medes, and N. F. Floyd (Lankenau Hospital Research Inst., Philadelphia). J. Biol. Chem. 166, 691-703 (1946). When C<sup>13</sup>-labeled acetate was oxidized by rat liver slices and rat kidney slices or minces in the presence of added *cis*-aconitate or citrate, the recovered citrate had no significant excess of C<sup>13</sup>, indicating that intermediates of acetate metabolism do not come into equilibrium with added tricarboxylic acids. However, when oxalacetate and acetoacetate, labeled with 6.48 atom % excess  $C^{13}$  in the  $\beta$  and carboxyl positions, were incubated aerobically with rat kidney homogenate, the citrate formed had a C<sup>13</sup> excess of 2.17% in the primary carboxyl carbons and a normal C<sup>13</sup> content in the other carbons. The formation of isotopic citrate is taken as positive evidence for the participation of the tricarboxylic acid cycle in fatty acid metabolism. Possible mechanisms are discussed.

THE METABOLISM OF a-,  $\beta$ -,  $\gamma$ -, AND  $\delta$ -KETO FATTY ACIDS IN MINCED TISSUE OF WARM-BLOODED ANIMALS. F. L. Breusch and R. Tulus (Univ. Istanbul, Turkey). Arch. Biochem. 11, 499-503 (1946). a-Keto acid (pyruvic acid) and  $\beta$ -keto acids ( $\beta$ -ketobutyric acid and  $\beta$ -ketocaprylic acid) disappear.  $\gamma$ -Ketovaleric acid (levulinic acid) and  $\delta$ -ketocaproic acid are not metabolized by any minced tissue. As shown in the reduction of oxaloacetic acid and the breakdown of citric acid there exist 2 groups of tissues: one, liver, kidney, muscle, brain and, pancreas, metabolizing aand  $\beta$ -keto acids, and a second group, lung, spleen, placenta, and embryonic muscle, unable to do so.

THE CARCINOGENICITY OF *p*-DIMETHYLAMINOAZOBEN-ZENE IN DIETS CONTAINING THE FATTY ACIDS OF HYDRO-GENATED COCONUT OIL OR OF CORN OIL. B. E. Kline, J. A. Miller, H. P. Rusch, and C. A. Baumann (Univ. Wisconsin, Madison). Cancer Research 6, 1-4 (1946). In rats fed synthetic diets containing 0.06% p-dimethylaminoazobenzene for 4 months and then dyefree diets for 2 more months, no liver tumors developed by 6 months when 2.4% of lauric or 4.7% of the fatty acids of hydrogenated coconut oil were fed in the diets. If, however, these lipides were replaced by 5% corn oil, 4.8% of the fatty acids of corn oil, 5%of olive oil, or by 4.5% oleic acid, the tumor incidences at 6 months were 80, 53, 33-53, and 87% respectively. On a diet free of added fat, 20% of the rats developed hepatomas by this time. CERTAIN EFFECTS OF DIETARY FATS ON THE PRODUCTION OF LIVER TUMORS IN RATS FED *p*-DIMETHYLAMINOAZOBENZENE. *Ibid.* 5-7. The incidence of liver tumors produced by feeding 0.06% p-dimethylaminoazobenzene in synthetic diets for 4 months (followed by 2 months of dye-free diet) was 23% when the diet was low in fat, as contrasted with 94, 53, 100, and 87% when the

diet contained 5% corn oil, 5% olive oil, 20% corn oil, or 20% Crisco or lard. (*Chem. Abs. 40*, 6636.)

GASTRIC LIPASE IN MAN. F. Schonheyder and K. Volqvartz (Aarhus Univ., Denmark). Acta Physiol. Scand. 11, 349-60 (1946). The optimum pH for gastric lipase (without CaCl<sub>2</sub>) activity with triglycerides of propionic, butyric, and caproic is 5.5-5.8, but shifts to the alkaline side with increasing number of C atoms (for triglycerides of capric, lauric, and stearic it is 7.2-7.9). Upon the addition of CaCl, to the system the lipase hydrolysis of trilaurin or tristearin at pH <7.0 is activated, and the optimum pH shifts 1.5-2.0 pH units to the acid side. Tributyrin is split by gastric lipase with the greatest initial velocity, but the activities toward solid triglycerides are very small. In an acid medium gastric lipase is very stable at 40°. In vivo experiments show that only lower triglycerides are appreciably split during the test period (25 min.). In children there is a tendency to split more rapidly cow butter fat than woman's milk fat. (Chem. Abs. 40, 6517.)

FATTY MATERIAL IN BACTERIA AND FUNGI REVEALED BY STAINING DRIED, FIXED SLIDE PREPARATIONS. K. L. Burdon (Baylor Univ. Coll. Med., Houston, Texas). J. Bact. 52, 665-78 (1946). An improved technic for demonstrating intracellular lipid in microorganisms by staining dried, fixed preparations with Sudan black B and counterstains is described.

MICROBIOLOGICAL FAT SYNTHESIS BY MEANS OF RHO-DOTORULA YEAST. L. Enebo, L. G. Anderson, and H. Lundin (Royal Tech. Univ., Stockholm, Sweden). Arch. Biochem. 11, 383-95 (1946). By drastic reductions in the supply of N and P during aerated cultivation of Rhodotorula gracilis the fat content of the yeast could be considerably increased. The minimum value for the N concentration in the substrate appears to be 0.6 g. N/100 g. glucose. In non-continuous cultivation on the 50-l. scale, fat contents of between 50 and 60% were obtained, the fat coefficient (Rippel) being 16-18. The generation time was 15-20 hours and the protein content amounted to only 12-13%. It is disadvantageous as regards sugar economy to extend the formation of fat over a long period as the fat coefficient gradually decreases. For the formation of 1 g. of fat in gracilis  $\pm$  4.5 g. glucose is required. When the supply of N and P was plentiful very short generation times were obtained (as low as 2.8 hours), but the fat contents in these cases were low. Continuous cultivation of gracilis with limited supplies of N and P proved to be unfavorable, as the generation time rose to 50-60 hours.

#### PATENTS

REFINING OIL. B. Clayton. U. S. 2,412,521. This is a continuous refining process using strong caustic as the refining agent and separating by means of centrifuges.

FATTY OIL DESLIMING PROCESS. W. A. Bush and E. A. Lasher (California Flaxseed Products Co.). U. S. 2,410,926. The process of de-sliming a fatty oil comprises mixing into the oil a substantially saturated water solution of sulfamic, oxalic, citric, picric, or maleic acids in an amount sufficient to break the slime dispersion, mixing into the mixture a solid filteraid powder in amount sufficient to absorb all of the water solution remaining after mixing with the fatty oil, and filtering out the filteraid, acid, and water with the slime from the purified oil. OLLS OF OLIVE, COCONUT, ETC. FLAVORS. J. H. Forkner. U.S. 2,411,201. The invention relates primarily to the treatment of fatty materials, such as refined edible oils and fats by infusion with a by-product, namely, presently discarded juice of certain products of plant origin, such as oil seeds or nuts to impart a desired flavor, color, and aroma to the refined oil.

PROCESSES OF REFINING, PURIFYING, AND HYDROGEN-ATING FATS, FATTY ACIDS, AND WAXES. I. Taussky. U. S. 2,413,009. In the process of refining crude tall oil is the step of subjecting an intimate mixture comprising tall oil, and a small percentage of a spent hydrogenation catalyst to  $H_2$  pressure of 50-750 lbs. per square inch at a temperature slightly above 212°F.

OIL SEPARATION METHOD FOR VITAMINIFEROUS PRO-TEIN MATERIAL AND THE LIKE. H. E. Crowther (Aquacide Co.). U. S. 2,413,692. The method of producing oil from fish liver material comprises coagulating the material, draining off free water, then comminuting to liberate the oil, adding water, and removing the floating body of oil.

CONCENTRATION OF FAT-SOLUBLE VITAMINS. L. O. Buxton (National Oil Products Co.). U. S. 2,412,561. The process depends on the preferential solubility of the vitamin in isopropanol and comprises dissolving the oil in the solvent and cooling until layering takes place.

PROCESS OF PRODUCING VITAMIN CONCENTRATES. L. O. Buxton (National Oil Products Co.). U. S. 2,412,-766. The vitamins in liver oils are concentrated by saponifying 60-95% of saponifiable material and extracting the unsaponified which contains the vitamins.

PECTIN PRODUCT. R. C. Nelson (Essential Oil Producers, Inc.). U. S. 2,412,282. Pectin is coated with fatty acids and amides of alcohol to make it water repellent and easily dispersible in water.

ALKYL ESTERS OF HIGHER FATTY ACIDS. F. H. Gayer and C. E. Fawkes (Continental Res. Corp.). U. S. 2,411,536. In the esterification of the fat acids of tall oil the amount of catalyst and reaction conditions are controlled to limit the esterification to the fat acids. The reaction is a preliminary step in the process of separating rosin acids from fat acids.

HIGH MOLECULAR POLYHYDRIC ALCOHOLS. E. W. Eckey and J. E. Taylor (The Procter & Gamble Co.). U. S. 2,413,612-13. These are esters of higher fatty alcohols and fat acid polymers containing 32-48 C atoms.

PROCESS FOR FINISHING TEXTILE MATERIALS, PARTICU-LARLY TO RENDER THE SAME WATER REPELLENT. E. Zerner, G. D. M. Davies, and P. I. Pollak (Sun Chemical Corp.). U. S. 2,413,024. A process of rendering textiles water repellent includes incorporating therein the reaction product of di-heptadecyl ketone and dodecyl amine, drying and baking at 130-150°.

INTERMEDIATE FOR PLASTICS OR DETERGENT MANUFAC-TURE. D. Swern (Sec. Agr.). U. S. 2,411,762. This invention relates to the oxidation product of oleyl alcohol and perbenzoic acid and has as its object the production of 9,10-epoxyoctadecanol.

INGREDIENTS FOR PRODUCING HIGH EXPLOSIVES. M. Bonotto. U. S. 2,411,145. A high-explosive ingredient consists of the nitrated solid compound resulting from the nitration of the oil-free, undenaturate solid product of the commercial solvent extraction of oil from the edible-oil group of oil-bearing seeds. DEFOAMER FOR THE SUGAR INDUSTRY. R. H. Larsen. U. S. 2,412,276. Fatty acids, recovered from  $H_2SO_4$  treated vegetable oil refining foots, are used as syrup defoamers.

CUTTING OIL. P. P. Gabriel. U. S. 2,412,082. The method of preparing a cutting composition comprises mixing approximately 88 lard oil, 12 S and 2 parts of pine oil by volume, adding to the mixture 25-40% by volume of  $CCl_4$  and storing the combined mixture in a closed container at room temperature of about 70°F. for a period of at least 2 weeks.

CUTTING OIL. T. W. Culmer (The Ohio Oil Co.). U. S. 2,412,131.  $\Lambda$  cutting oil compounded from chlorinated sulfurized sperm and petroleum oils from which under conditions of normal use active S breaks out, contains 0.5-1.0% lecithin to prevent such active S from causing stains.

ANTIFRICTION BEARING LUBRICANT. A. J. Morway and A. Beerbower (Standard Oil Development Co.). U. S. 2,411,587. An unctuous, transparent anhydrous grease contains .03-.06% free alkalinity as NaOH and is composed of mineral lubricating oil thickened to smooth grease consistency with a mixture of Na and Zn soaps in which the ratio of Na to Zn soap is between 14:1 and 28:1. POUR DEPRESSORS FOR LUBRICANTS. E. Lieber (Standard Oil Development Co.). U. S. 2,412,589. The product is an aromatic-kerosene formaldehyde resin which has been condensed with amyl chloride at a temperature above  $125^{\circ}$ F.

LUBRICANTS. M. L. Schwartz (Standard Oil Co.). U. S. 2,412,633-4. A corrosion inhibitor for mineral oil lubricants contains soap, petroleum sulfonates, castor oil or monoricinoleate, and sulfurized terpene.

LUBRICANT GREASE. L. G. Vande Bogart and R. W. Manuel (Crane Co.). U. S. 2,412,929. The grease comprises castor oil 5-45%, petroleum oil 5-45%, lower alkyl phosphate 0.5-5.0%, and a mixture of bentonite and lithopone, the remainder.

LUBRICANT CONTAINING ALKYL PIPERIDINE SALTS. G. E. Barker (Elgin Natl. Watch Co.). U. S. 2,412,-956. The lubricant consists of an organic lubricant liquid having dissolved therein 0.5-1.0% of an alkylpiperidine salt of a fatty acid.

RUST-INHIBITING LUBRICANT. W. R. Turner (The Atlantic Refining Co.). U. S. 2,413,852. The lubricant comprises hydrocarbon oil and a rust-inhibiting quantity of an oil-soluble reaction product of a fat acid phosphate and a branched-chain alkylamine containing from 4-16 C atoms in the alkyl group.

### Abstracts

# **Drying Oils**

#### Edited by HOWARD M. TEETER

VULCANIZED LINSEED OIL. STUDY OF THE POLYMERI-ZATION REACTION BY MEANS OF X-RAYS. J. J. R. Engel (National Univ., La Plata, Argentina). Revista Facultad Ciencias Quimicas 19, 41-55 (1944). Samples of vulcanized linseed oil were prepared by heating linseed oil with flowers of S at 140° (products contained 10, 20, 30, and 40% of combined S) and by cold vulcanization with  $S_2Cl_2$  (products contained 15 and 30% of combined S). Examination of the X-ray diffraction patterns of these samples gave results which indicate that vulcanized linseed oil consists of units comprising 3 sulfurized glyceride molecules joined in zig-zag fashion through S. The over-all length of the unit is 13 Å or, in more fully vulcanized samples, 10.8 Å.

POLYMERIZATION AND DRYING OF OILS AND ESTERS OF FAT ACIDS. VII. THEORY OF SOLIDIFICATION AND DRY-ING OF OILS AND ESTERS OF FAT ACIDS. A. Ya. Drinberg. J. Applied Chem. (U.S.S.R.) 19, 251-7 (1946). Solidification is an intermolecular reaction and in part an intramolecular reaction. At low temperatures, solidification results from autoxidation and polymerization of peroxides. At high temperatures, solidification results from oxypolymerization and polymerization. Tridimensional, insoluble polymers are formed whose O content decreases with the temperature of the reaction. The growth of these polymers is proportional to the number of double bonds and independent of their position. VIII. THEORY OF AGING OF FILMS. Ibid. 258-61. Films of oils or fat acid esters consist of a solid and a liquid phase. The reaction of the liquid phase with atmospheric  $O_2$  is analogous to oxidation of liquid oils. It decreases the elasticity of the film. The solid phase, consisting of macromolecules,

cannot further polymerize through the introduction of active O; hence cleavage occurs at the places of the original double bonds. Aging is affected also by instability of the gel of the film owing to an excess of liquid phase; this leads to syneresis. The problem of obtaining durable nonaging films consists in (1) synthesis of fast drying esters of unsaturated acids having a low number of unsaturated bonds and (2) determination of the conditions of drying under which the unsaturated groups would be used up mainly in the process of drying. (Chem. Abs. 41, 1113.)

CATALYTIC ISOMERIZATION OF VEGETABLE OILS. S. B. Radlove, H. M. Teeter, and J. C. Cowan (Northern Reg. Res. Lab., Peoria, Ill.). Official Digest Fed. Paint Varnish Prod. Clubs 265, 74-84 (1947). Soybean and linseed oils are isomerized by heating at 160-170° with a catalyst composed of reduced Ni deposited upon carbon black. The isomerized oils have low acid values, colors, and viscosities, and they contain approximately 30% conjugation measured spectrophotometrically. Details are given of the preparation of the catalyst, selection of the carbon black, effect of metals upon catalyst activity, and variation in conjugation obtained with various grades of soybean oil. Samples of catalyst may be used to isomerize up to 10 batches of oil before exhaustion. Results of preliminary evaluation of the isomerized oils in paints, varnishes, and alkyd resins are reported. Bodying rate of isomerized linseed oil equals or exceeds that of dehydrated castor oil. Bodying rate of isomerized soybean oil is comparable to that of alkali-refined linseed oil. Paints made with isomerized soybean oil develop considerable after-tack in conventional formulations. This defect can be overcome by the addition of 5-11% of CaO to the pigment. Behavior of these lime-containing paints upon accelerated weathering is excellent.

SODIUM REDUCTION OF FATTY ACID ESTERS. V. L. Hansley (E. I. du Pont de Nemours and Co., Inc., Niagara Falls, N. Y.). Ind. Eng. Chem., 39, 55-62 (1947). The preparation of fatty acid alcohols by catalytic hydrogenation of fatty acid esters requires a high pressure and temperature, does not produce high yields of unsaturated alcohols, and, in the case of triglycerides, prevents recovery of the valuable glycerine which is produced in the reaction. The Na reduction of fatty acid esters to alcohols has none of these disadvantages, and improvements in the method have increased the Na efficiency of the reaction and the reaction rate, while decreasing the amount of condensation byproducts and the amount of alcohol required. Certain secondary alcohols have been found the most efficient reducing alcohols, since they react with Na less than the primary alcohols and produce less bimolecular reaction products than the tertiary alcohols. The introduction of a selected hydrocarbon solvent into the reaction helps remove the heat generated, by its refluxing action, controls the reaction temperature, and helps to prevent gelation of the reactants. The reaction is carried out in 2 stages. The mixture of fatty acid esters, reducing alcohol, and hydrocarbon solvent is slowly added to Na dispersed in additional solvent. The Na alkoxide mixture formed is then slowly added to hot water to generate the free alcohols. High yields and reaction efficiencies are shown by material balances and H<sub>2</sub> evolution measurements. Triglycerides are easily reduced by this method, while Me esters are less reactive with

few exceptions. Highly unsaturated alcohols from marine oils can be prepared and rosin acid yields abietyl alcohol with drying properties. Nitriles may be reduced to the corresponding amines.

COMPARATIVE OXIDATION OF LINSEED AND SARDINE oils. G. A. O'Hare and W. J. Withrow (Congoleum-Nairn, Inc., Kearny, N. J.). Ind. Eng. Chem. 39, 101-4 (1947). Improved blowing technics, which are not described, were used to obtain a high ratio of uptake to O<sub>2</sub> degree of polymerization when sardine and linseed oils were blown with air at 220°F. Relatively small increases in viscosity and refractive index indicated low degrees of polymerization during blowing, and the rate of increase in these constants was greatest toward the end of the blowing period. It is shown that the increase in dielectric constant is small when linseed oil is heat-bodied, but increases in proportion to oxygen uptake when the oil is blown, thus proving its sensitivity to oxidative changes. This constant is a satisfactory control measurement in the production of oxidized oils.

The change in refractive index, specific gravity, and other conventional drying oil constants during blowing at 220°F. is similar for linseed and sardine oils. Ultimate analysis, however, shows that the  $O_2$  content of sardine oil during blowing follows a broken curve indicating that certain periods of oxidation are followed by periods of deoxidation. The deoxidation is postulated as being due to breakdown of unstable O linkages accompanied by polymerization or condensation and elimination of volatile products containing oxygen. Samples of sardine oil removed during blowing at periods just preceding deoxidation were found to heat-body very rapidly.

## Abstracts

## Soaps

DETERMINATION OF THE INDUSTRIAL VALUE OF DE-TERGENTS. II. METHODS TO DETERMINE THE SCALE-REMOVING POWER AND THE DISPERSING POWER TOWARD CALCIUM SOAPS. J. P. Sisley. Corps gras, savons 2, 77-9 (1944). The difference among various deter-gents in scale-removing power and effect on the dispersion of lime soaps was determined by 4 empirical methods: The amount of detergent necessary to create a permanent foam in a Ca soap solution, the amount of detergent required to remove the turbidity from a Ca soap solution, the amount of Ca salts remaining in a filtered mixture of detergent and Ca soap solution determined by titration with dilute HCl, and the behavior of certain vat dyes (especially Solanthrene Blue NB) which are very sensitive to the hardness of an aqueous system. These methods are comparative rather than absolute. It is stressed that if softened or purified water was used more in industry, soap would retain its preeminence and detergents would be reserved for special applications. (Chem. Abs. 41, 874.)

A STUDY IN DETERGENCY. Sawyer F. Sylvester, et al. Am. Dyestuff Reptr. 36, 91-6 (1947). A study has been made with the Detergency Comparator to compare the scouring efficiency of soap and synthetic

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anionic, nonionic, and cationic detergents, namely an alkyl aryl sulfonate, polymerized organic alcohol, and a polyethylene ether of a fatty amine. The variables studied were bath to cloth ratio, and additions of Na<sub>2</sub>CO<sub>3</sub>, NaHCO<sub>3</sub>, Na<sub>2</sub>SO<sub>4</sub>, and H<sub>2</sub>SO<sub>4</sub>. Na<sub>2</sub>CO<sub>3</sub> appeared to be the best assistant with the detergents tested although all of the salts proved to be of value. Their effect may be to drive the detergents to the oil-water interfaces. Standard soil used consisted of 50% mineral oil and 50% grease oil with the addition of lampblack. Results showed that 10% of each detergent with 6% of Na<sub>2</sub>CO<sub>3</sub> give an initial pH of about 11.0 and produce excellent overall results in oil and lampblack removal.

THE CONSTITUTION OF SULFATED OILS. I. METHODS FOR DETERMINING THE —COOH, —OSO<sub>2</sub>OH, and —SO<sub>3</sub>H GROUPS AND THEIR SALTS. D. Burton and L. F. Byrne (Wm. Walker & Sons, Ltd., Bolton, Eng.). J. Intern. Soc. Leather Trades Chem. 30, 306-15 (1946). Sulfated oils may contain carboxyl, alkyl sulfate, and sulfonic acid groups, free or partly neutralized with Na or K, NH<sub>4</sub>, or Na and NH<sub>4</sub>. By a preliminary determination of pH value of a 1% emulsion, oils are separated into 2 classes: (1) those of pH higher than 4, in which all alkyl sulfate and sulfonic acid groups together with part of the carboxyl groups have been neutralized, and (2) those of pH less than 4, containing free -OSO<sub>2</sub>OH or -SO<sub>3</sub>H groups and possibly some free mineral acid. By determining the neutralizing agent each class is further subdivided. This paper covers analysis of Class 1 oils neutralized with Na. Free COOH: titrate with 0.1 N alcohol KOH in  $Et_2O$ -EtOH to the phenolphthalein end point. COONa: acidify with 25 ml. 0.5 N HCl and backtitrate with 0.5 N NaOH to the thymol-blue end point. OSO<sub>2</sub>ONa: decompose 8 g. by vigorously boiling for 1 hr. under reflux with 25 ml. N H<sub>2</sub>SO<sub>4</sub>, cool, add 20 ml. Et<sub>2</sub>O, 100 ml. H<sub>2</sub>O, 30 g. NaCl, and 5 ml. of 0.1% bromophenol blue. Titrate with 0.5 N NaOH with vigorous shaking until the aqueous phase turns red. Deduct the acid equivalent to the COONa from the total acid taken and subtract the remainder from the total alkali titration to obtain the volume of alkali required to neutralize NaHSO<sub>4</sub> formed by hydrolysis of  $-OSO_2ONa$ .  $SO_3Na$ : carry out a Procter-Searle determination as for mineral acid in leather. To the acid value found, add the acid equivalent of the -COONa and deduct the acid equivalent of the -OSO<sub>2</sub>ONa previously found. Na<sub>2</sub>SO<sub>4</sub>: determine total sulfate in an aliquot of the solution resulting from the Procter-Searle determination and deduct sulfate equivalent to the -OSO<sub>2</sub>ONa, the -SO<sub>3</sub>Na, and the volume of standard  $H_2SO_4$  used in the Procter-Searle determination. NaCl: determine chlorides volumetrically in an aliquot of the solution resulting from the Procter-Searle determination. (Chem. Abs.

41, 1117.) Phase study of commercial soap-alkaline elec-TROLYTE WATER-SYSTEMS. Reynold C. Merrill (Philadelphia Quartz Co.). Ind. Eng. Chem. 39, 158-66 (1947). A phase study of commercial mixed soapwater-electrolyte systems was made using NaCl and 9 salts industrially important as soap builders. The data cover soap concentrations to 50%, electrolyte concentrations to 27%, and temperatures to 180°. The salts used were NaCl, Na<sub>2</sub>CO<sub>3</sub>, Na tetraborate, Na<sub>3</sub>PO<sub>4</sub>, Na<sub>4</sub>P<sub>2</sub>O<sub>7</sub>, Calgon, Na metasilicate, Na silicates of SiO<sub>2</sub>/Na<sub>2</sub>O ratios by weight of 2.46 and 3.93, and a K silicate of  $SiO_2/K_2O$  ratio by weight of 2.04. The solubility of the soap in solutions of these salts and their effect on the transition from crystalline to liquid crystalline soap varies widely both on weight and molecular bases. The order of increasing effect differs with concentration and temperature; however, sufficient regularities exist to enable predictions to be made of the phase diagrams for other soaps and at other concentrations.

CRYOSCOPIC EVIDENCE FOR MICELLAR ASSOCIATION IN AQUEOUS SOLUTIONS OF NON-IONIC DETERGENTS. Emanuel Gonick and James W. McBain (Stanford University, California). J. Am. Chem. Soc. 69, 334-6 (1947). Measurements of freezing point lowerings of aqueous solutions of 3 non-ionic detergents of the polyethylene oxide-hydrocarbon type show that these compounds are characterized by micelle formation, a "critical concentration" for the formation of micelles, expansion of the micelle structure with dilution, and a comparable power of solubilization. The phenomena are uncomplicated by ionization.

Some measurements of the streaming double REFRACTION OF SODIUM OLEATE. Olle Snellman. Arkiv Kemi, Mineral Geol. B19, No. 5, 1-7 (1944). The streaming double refraction of Na oleate solutions ranging in concentration of 4-12% was investigated in the Kundt rotation apparatus used by Snellman and Bjornstahl. Solutions containing less than 6% Na oleate showed no measurable double refraction. At 24° the extinction angle (measured from a direction  $45^{\circ}$  to the direction of flow) decreased from  $27^{\circ}$ for a 6% solution to  $2\frac{1}{2}^{\circ}$  for a 9% solution. The extinction angle increased with increasing velocity gradient (G). The double refraction was negative, and also increased with G. For an 8% solution at 24° the phase difference  $(\Delta)$  was  $0.7^{\circ}$  at G = 400, and  $2.6^{\circ}$  at G = 2400. Increasing temperature reduced both the amount and the rate of increase of  $\Delta$  with G. At concentrations above 8%,  $\Delta$  increased rapidly, going from 2.6° for an 8% solution at 24°, G = 2400, to 17° for a 9% solution. The results can be explained by assuming that the formation of large crystalline micelles does not occur at a definite concentration but over the broad range from 6 to 10%. At higher temperatures, the transition range is displaced toward higher concentrations. (Chem. Abs. 41, 900.)

#### PATENTS

HELICAL GRAIN SOAP. James Garvey, Arthur Garvey, and Horace Garvey. U. S. 2,414,098. Soap cake is manufactured with a helical grain throughout as contrasted to a longitudinal grain; thus it has little tendency towards wet cracking and keeps shape well.

NON-IRRITANT DETERGENT. Joseph Cunder (National Oil Products Co.). U. S. 2,414,452. A mild nonirritating soap consists of a sulfated oleic acid and an alkali metal soap of a saturated fatty acid.

STABILIZED SOAP. Myers F. Gribbins (E. I. du Pont de Nemours & Co.). U. S. 2,416,052. Soap is stabilized by adding a substituted  $\beta$ -mercaptopropionic acid or ester, prepared by the addition of mercaptan to acrylonitrile.

PREPARATION OF HEAVY METAL SOAPS. Arthur G. Weber and Clement H. Hamblet (E. I. du Pont de Nemours & Co.). U. S. 2,416,074. Heavy metal (Pb) soaps of fatty acids are prepared by reacting esters of the higher fatty acid with the heavy metal while bubbling  $O_2$  through the liquid acid at a temperature between 50 and 200°.

LITHIUM COMPOUNDS IN DETERGENTS. (Mathieson Alkali Works, Inc.). British 581,946. Water-soluble polyphosphates are added to Li soap solutions to prevent precipitation of the soap.

SURFACE ACTIVE AGENTS. E. Zerner and W. Kaplan (Sun Chemical Corp.). U. S. 2,413,161. Aromatic compounds are condensed according to the Friedel-Crafts synthesis and then sulfonated.

DETERGENT COMPOSITION FOR USE IN HARD WATER. F. C. Bersworth. U. S. 2,412,943. A detergent composition for use in very hard water and in water containing moderate amounts of strong electrolytes, consists of soap and about 10% of the acid-trialkali metal salt of ethylene diamine tetracarboxylic acid.