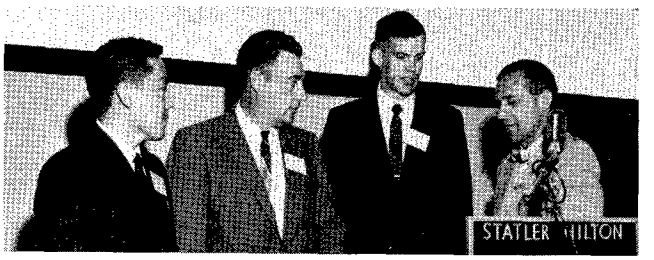
Program Features Gas Chromatography

AN EXCELLENT technical program, well organized by the program committee chaired by Roslyn Alfin-Slater of the University of Southern California, profoundly pleased the large attendance at the 33rd fall meeting of the American Oil Chemists' Society in Los Angeles, Calif., September 28–30, 1959, at the Statler Hilton hotel. Fifty-six papers were presented in nine technical sessions, covering almost all of the important phases of fats and oils, such as processing, chemistry, analysis, detergents, coatings, polymers, and nutrition. Highlighting the technical program however were special sessions on gas chromatography and soaps and syndets. Authors of technical papers came from 13 states, District of Columbia, and two foreign countries. The Society succeeded also in attracting more universities to participate in the technical program. Nine technical papers of this meeting were contributions from seven universities. The rest of the papers were given by speakers from three foreign laboratories, 11 research institutes and government laboratories, and 14 industrial laboratories.

Chromatography of Mono- and Diglycerides in Gas Phase

Quantitative estimation of mono-, di-, and triglycerides derived from hydrogenated coconut oil by gas chromatography was reported by V. R. Huebner of Armour and Company. The components were separated in a three-foot column, packed with silicone rubber-coated Celite. The



GAS CHROMATOGRAPHY—Speakers at this opening session at the 33rd fall meeting of the American Oil Chemists' Society are Tao-Zuen Chu, B. M. Craig, V. R. Huebner, with the chairman, James Mead.

column temperature was gradually increased from 250° to 370°C. during the analysis. B. M. Craig of the National Research Council, Canada, described the quantitative determination of short chain (C_3–C_9) fatty acids by gas chromatography. The acids were converted into butyl or phenacyl esters, and the esters were then separated on a silicon column. The quantitative analysis of fatty alcohols by gas chromatography was made possible by the use of a Ucon polar column. Tao-Zuen Chu of Wilkens Instrument and Research Inc. reported that direct analysis of fatty alcohols without converting into their acetates can be made with a 15-inch column at 160–220°C. Mr. Chu also reported on his extensive comparison of the polyester substrates for separating fatty acid methyl esters. A new ester, coded XYZ, was reported to have excellent resolution as well as exceptionally good thermal stability. Unfortunately Mr. Chu was not allowed to announce the chemical structure and manufacturer of this new substrate. In spite of the higher plate efficiency of the butanediol succinate column, the diethyleneglycol succinate column was recommended for the separation of C-18 unsaturated fatty esters because of its high resolution.

Potential Uses of Diglyceride Esters of Dibasic Acids

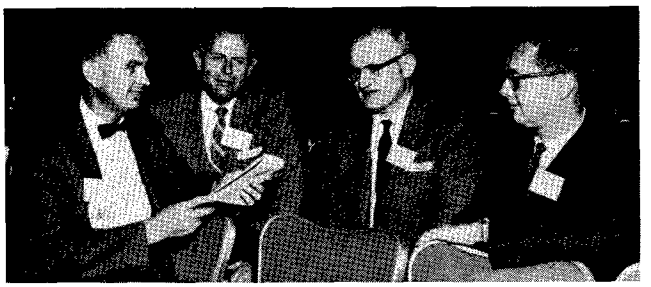
The potential uses of the series of compounds formed by esterification of diglycerides with succinic, adipic, and

SOAPS AND SYNDETS—Session B speakers Monday morning are *(left to right)* L. E. Weeks, J. K. Weil, John Morrisroe, chairman, R. L. Liss, F. G. Villaume, and L. W. Burnette.

other short-chain dibasic acids were discussed by R. O. Feuge, Southern Regional Research Laboratory. The solid esters are comparable to carnauba wax in hardness. They are better than completely hydrogenated cottonseed oil in their ability to thicken a vegetable oil. Rosemary L. Shull of the University of Southern California reported that both the adipic acid-peanut oil fatty acid polyester and the adipic acid ester of peanut oil diglycerides had a digestibility coefficient well over 80% when fed to rats at a level of 15% in the diet. The absorption and oxidation of the stearic acid moiety in this type of esters were found to be similar to those previously observed in other synthetic stearic acid-C^{14} containing triglycerides. J. J. Spadaro, Southern Regional Research Laboratory, reported the pilot-plant study of preparing a cocoa butter-like fat by the random interesterification of completely hydrogenated cottonseed oil with olive oil, followed by crystallization from solvent.

A continuous process for caustic refining of crude coconut oil in a completely pressurized system was presented by F. E. Sullivan, DeLaval Separator Company. The development of new types of filters for the decolorizing, deodorizing, and winterizing of oil during the filtration cycle or as a separate cycle was reported by J. B. Levy, Sparkler Manufacturing Company. Full automation can be applied to this new method of operation. J. J. Spadaro, Southern Regional Research Laboratory, applied the filtration-extraction process now in commercial operation on cottonseed to the extraction of liquid wax from jojoba seed. T. H. Little, Sharples Corporation, reported the use of an horizontal solid-bowl type of continuous centrifuge and a "chemical collector" to produce highly-clarified tallow products. The self-cleaning disc centrifuge was reported to have wide applications, not only in the upgrading of tallow and grease but also in the purification of trap grease and emulsified fat and water streams.

BIOCHEMISTRY AND NUTRITION—In this line-up are H. S. Olcott, Hans Kaunitz, Cecil Entenman, chairman, N. R. Di Luzio, R. P. A. Sims, John Togashi, and N. D. Embree.



SOAPS AND SYNDETS cont.—Speakers at this continuing session include L. O. Leenerts, chairman, J. C. Harris, W. M. Linfield, and W. C. Powe.

Synergistic Effects Between Substances Containing Amino Groups and Phenolic Antioxidants

H. S. Olcott, University of California, demonstrated the unusually effective synergism in fish oils, lard, and purified fatty esters between substances containing such amino groups as proline, phospholipids, and tri-iso-octylamine and phenolic antioxidants. In some cases an interaction of antioxidants with amino substances is indicated by infrared absorption spectrophotometry. Antioxidants having an unsubstituted carbon atom in the benzene ring ortho to the hydroxyl group are more effective synergists with amino compounds.

H. J. Togashi, Quartermaster Food and Container Institute for the Armed Forces, reported that the oxidation of lipid films was dependent on the chemistry of the surface. The effectiveness of antioxidants is less on surfaces than in bulk. High concentrations of phospholipid were found to inhibit the surface-oxidative mechanism. This study of the oxidation of lipid films is of great importance to fat deterioration of the dehydrated food because of the creation of new surfaces during the dehydration. E. N. Frankel, Northern Regional Research Laboratory, reported that, when autoxidized fatty esters were heated in the absence of oxygen at 210°C., the principal product was dimers of the fatty acids. Dimerization of the hydroperoxides was postulated as occurring through alkyl free radicles to give carbon-to-carbon linkages. The dimers are not cyclic in nature.

J. G. Willard, Southwest Research Institute, reported that, in the hydrogenation of linseed oil, higher Rufert nickel catalyst concentrations favored hydrogenation of linolenic acid in preference to less unsaturated acids. The initial reaction in the hydrogenation of pure methyl linolenate strongly favors the 12 position. The variables of catalyst, catalyst concentration, solvent, temperature, and pressure have very little effect on the selectivity. L. F. Albright, Purdue University, studied the solvent hydrogenation of cottonseed oil. He reported that solvent and nonsolvent hydrogenation runs at comparable conditions had essentially the same selectivity and isomerization.

High Levels of Saturated Fats and Lipogranuloma in Rats

N. D. Embree, Distillation Products Industries, reported that prolonged feeding, to rats, of high levels of various saturated fats along with low levels of unsaturated fats has led to lipogranuloma in some of the fat cells. This effect was reversed by changing to a diet less rich in saturated fats and was prevented, even at high levels of saturated fat, by including an equal level of unsaturated fat. G. D. Michaels, Institute for Metabolic Research, described studies carried out in normal and abnormal human subjects under quantitatively-controlled conditions with respect to dietary intake. Analyses of plasma lipids showed that the triglycerides and the unesterified fatty acids are the first to reflect the composition of the dietary fat. In a short time the composition of the cholesterol esters is changed very appreciably. In some instances, during the feeding of fish oil which contains no arachidonic acid, this acid appears in appreciable quantities in one or more of the plasma lipid fractions. David Kritchevsky, Wistar Institute of Anatomy and Biology, reported that cholesterol administered in the absence of added fat to rabbits is more atherogenic than when it is fed together with corn oil. Furthermore cholesterol dissolved in the corn oil prior to mixing with the diet is more atherogenic than when it is merely suspended in the oil.

Hans Kaunitz, Columbia University, further studied the toxic effects of feeding cottonseed oil aerated at 95°C. for 300 hrs. to rats. He emphasized that human dietary fat rarely reaches such a high degree of autoxidation. Medium-chain, saturated triglycerides, and cottonseed oil consistently improved the depressed growth and minimized liver and kidney enlargement; long-chain, saturated triglycerides, and beef fat did the reverse.

Raymond Reiser, Texas Agricultural Experiment Station, described the dynamic state of tissue lipids by feeding tripalmitin labelled with C^{14} in both the glycerol and fatty acid moieties. After 12 hrs. the glycerol in adipose tissue and liver triglycerides disappears at a faster rate than the fatty acids. Between the third to twelfth hours however, fatty acids enter adipose tissue, triglycerides at a higher rate than glycerol, and the liver triglycerides at a lower rate. Similar results were found in the blood lipids and in liver lecithin and cephalin. R. P. A. Sims, Department of Agriculture, Canada, reported on the gross changes in total lipid in flax and safflower seeds and tissue as the plants progress from fertilization to maturity by tagging the plants at flowering and collecting samples at intervals of approximately 10 days. The accomplishment of complete detoxification of the ricin of castor bean by moist cooking, with or without alkali, and substantial reduction in the allergenic response of castor meal was reported by E. A. Gastrock, Southern Regional Research Laboratory.

Nuclear Spin Resonance, a New Analytical Tool for Fatty Acids

A Varian model V-4300 C 60-megacycle per second nuclear spin resonance spectrometer with the associated Varian 60 high resolution 12-inch magnetic system was used by George Pish, Southwest Research Institute, to analyze the *cis* isomers resulting from the hydrogenation of linolenic acid. The paper read by J. G. Willard showed great potential for this new technique for quantitative determination of the position of double bonds in polyunsaturated fatty acids. O. S. Privett, Hormel Institute, described the isolation of methyl linoleate, linolenate, arachidonate, eicosapentaenoate, and docosahexaenoate in highly purified form by the use of adsorption and reverse-phase partition chromatography. M. L. Peterson, Rockefeller Institute, applied an amperometric technique to the measurement of peroxides in lipids by the peroxide-iodide reaction to measure as low as 10^{-8} to 10^{-9} equivalents of peroxide in a sample of lipids. The end-point, an abrupt change in current flow measured by a conventional pH meter in the electrical circuit, is apparent when 10^{-13} equivalents of iodine are present. L. J. Morris, Hormel Institute, reported a simple method for the detection and estimation of epoxy acids by measuring the infrared absorption near 2.8 microns before and after converting the epoxide ring to a vicinal dihydroxide. R. P. A. Sims, Department of Agriculture, Canada, studied the alumina column chromatography for separation of polar and nonpolar lipids.

ANALYSIS AND GENERAL—G. B. Oberg, chairman, is shown with O. S. Privett, L. J. Morris, R. O. Feuge, M. L. Peterson, Rosemary L. Shull, G. D. Michaels, and (on the other side of the blackboard) David Kritchevsky, who had missed out on the picture of the biochemistry session speakers.

CHEMISTRY AND PROCESSING—G. W. Busby, chairman, ranges his speakers thus: F. E. Sullivan, E. A. Gastrock, Constance Willard Gould, J. J. Spadaro, and John G. Willard.

When the phospholipid concentration is low, the conditions set by the 1956 Technical Committee of the N.S.P.A. for the chromatography of linseed oil gave the most complete separation.

L. E. Weeks, Monsanto Chemical Company, developed an analytical scheme for the quantitative isolation and identification of the various components of surfactant mixtures, following their removal from detergent compositions. Surfactant mixtures from both built and unbuilt liquid and solid detergent compositions were successfully analyzed by this scheme.

The resistance to freezing and thawing of fat emulsions for intravenous alimentation was studied by W. S. Singleton and reported in a paper read by R. O. Feuge, Southern Regional Research Laboratory. The rate of thawing was more critical with respect to increase in particle size than the rate of freezing; a slow rate of thawing caused the least increase in particle size. Emulsions prepared from oils of lower melting point, *i.e.,* safflower oil and solvent-fractionated cottonseed oil, exhibited greater stability in regard to freezing and thawing.

Deodorant Activity Not Correlated to in vitro Bacteriological Data

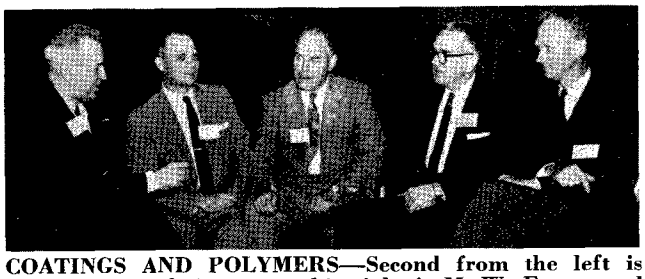
W. M. Linfield, Armour and Company, reported that the antibacterial agent contained in deodorant soaps can accomplish considerably more than deodorant activity. Certain pairs of antibacterial chemicals exhibit synergism which cannot be explained on the bases of chemical structure alone. Small amounts of nonionic detergents tend to activate soap germicides whereas large amounts tend to neutralize them. The deodorant activity was found to show no correlation to *in vitro* bacteriological data. This points out that laboratory *in vitro* methods of screening antibacterial agents are not necessarily reliable guides for potential deodorant activity. The same author also reported in another paper that the use of an antibacterial fabric-softener in institutional laundries produces a substantial reduction of the over-all bacterial load of the soiled linens. A cationic softener proved to be an excellent carrier for a mercurial agent and a successful agent in the treatment of linens in the laundry.

The contamination of N-methyltaurine by salt as prepared classically by the Schotten-Baumann condensation was avoided by L. W. Burnette, General Aniline and Film Corporation, by the use of excess fatty acids. The residual fatty acid in the product is a natural and useful component for mixed soap synthetic bars. Amides of *alpha*-sulfonated fatty acids were prepared by J. K. Weil, Eastern Regional Research Laboratory. Their detergent and other surface-active properties were reported. W. C. Schar, Enjay Laboratories, said that the sulfated tridecyl ethoxylates appear to give optimum foam stabilization when containing four to five moles of ethylene oxide. These ethoxylates were reported to give better performance in dishwashing over a wider range of water hardness than do the other ethoxylate sulfates.

A New Family of Bleaching and Sanitizing Products, the Chloro-isocyanuric Acid Compounds

R. L. Liss, Monsanto Chemical Company, discussed the applications of the chloro-isocyanuric acid compounds in bleaching and sanitizing products for consumer and industrial use. F. G. Villaume, American Cyanamid Company, indicated that the optical bleaches currently being incorporated in soaps and detergents produce a considerably-reduced whitening effect on wash-and-wear cotton as compared with untreated cotton. The fastness properties of these optical bleaches are also different on wash-and-wear from untreated cotton.

The organic soil that had gradually accumulated on cotton garments was extracted and analyzed by W. C. Powe, Whirlpool Corporation. The fatty acid composition of clothes soil is similar to sebum and is remarkably uniform from a variety of sources. J. C. Harris, Monsanto Chemical Company, commented on a very important feature of tripolyphosphate besides its sequestrant water-softening action and its detersive effectiveness. Tripolyphosphate was found to adsorb on a glass surface and reduce the tenacity of subsequent fatty resoiling. This may account to a considerable degree for the demonstrated high practical cleansing effectiveness of the compound.



COATINGS AND POLYMERS—Second from the left is R. O. Feuge, chairman; at his right is M. W. Formo and at his left, O. S. Privett, E. L. Patton, and E. F. Carlston.

Voltolization of Linseed Oil and Polymers of New Chemical Structure

The polymerization product obtained by treating linseed oil with an electric discharge in a hydrogen atmosphere showed a completely different chemical structure from that of thermally or catalytically polymerized linseed oils. Herman Mader, Laboratory of Chemical Technology, Holland, reported that voltolized linseed oils contain only small amounts of cyclic compounds. Their viscosity is relatively low, even at a high polymerization degree. E. F. Carlston, California Research Corporation, revealed the commercial possibilities of incorporating vegetable and marine oils into alkyd resins by an acidolysis procedure whereby the oil is heated with a phthalic acid at a temperature high enough to cause an interchange reaction and the formation of a mixture of monobasic acids, which are then esterified with a polyhydric alcohol. Since orthophthalic acid dehydrates to the anhydride at the temperatures required for

CHEMISTRY AND PROCESSING cont.—These four are Harold K. Latourette, R. L. Olson, J. B. Levy, and Donald Jackson.

the acidolysis reaction, it is of great interest for the production of isophthalic and terephthalic alkyd resins.

E. L. Patton, Southern Regional Research Laboratory, reported that the method of L. L. Hopper and co-workers for preparing tung oil varnishes, using zinc resinate as a gel inhibitor, is adaptable for large-scale commercial use. The total production costs including financing and sales costs were estimated to be $1.27 per gallon at an annual production of 6,800,000 gallons and $1.50 per gallon at an annual production of 100,000 gallons.

W. J. De Tarlais, Northern Regional Research Laboratory, said that heteropolymers of nonconjugated linseed vinyl ether with 1-methoxy-1,3-butadiene and with vinyl ethers of a number of alcohols showed little improvement in coating properties over homopolymers. Baked films of butylphenoxyethyl vinyl ether-nonconjugated linseed vinyl ether copolymers were found to have greatly-improved alkali resistance. The same author also reported that polyunsaturated fatty vinyl ethers can be prepared without inducing conjugation by de-alcoholizing acetals, which were prepared from nonconjugated linseed oleyl and stearyl alcohols by the acid-catalyzed addition of the alcohols to ethyl vinyl ether. Another method for the preparation of nonconjugated linseed vinyl ether was reported by O. L. Brekke, Northern Regional Research Laboratory. By transetherification of linseed alcohol with vinyl ethyl ether, 93% or better conversion in one step was obtained.

A Completely Continuous Countercurrent Process of Epoxidation

H. K. Latourett, Food Machinery and Chemical Corporation, spoke about a novel continuous countercurrent epoxidation process with the use of well-designed colored slides. H. P. Dupuy, Southern Regional Research Laboratory, described the preparation of 12-ketostearic acid from castor oil, and 4-ketostearic acid from oiticica oil with the subsequent preparation of their vinyl esters. Infrared analyses revealed that lactonization of the 4-ketostearic acid occurred during the hydrogenation of the oil and during the vinylation of the keto acid.

Aliphatic urethans were prepared by M. W. Formo, Archer-Daniels-Midland Company, with amines and alcohols of high purities. The urethans give thixotropic gels with mineral oil, soybean oil, solvent-thinned resins, and similar materials at concentrations as low at 0.5%. In general, better defined crystal structure and poorer thixotropic properties were observed with an increase in symmetry. A study of the preparation of dibasic acids by autoxidation of oleic acid under pressure was reported by Constance W. Gould, Stanford Research Institute. The maximum total yield of C_7–C_{10} dibasic acids was 15–20% by weight of the oleic acid charged. O. S. Privett, Hormel Institute, showed that the formation of chromophores which cause the yellowing of protective coating does not require the presence of molecular oxygen. The color bodies isolated from yellowed protective coating are soluble in both aqueous alkaline solution and organic solvents. The formation of the chromophores in protective coatings can be effectively inhibited by the incorporation of such aliphatic aldehydes as butyl aldehyde.

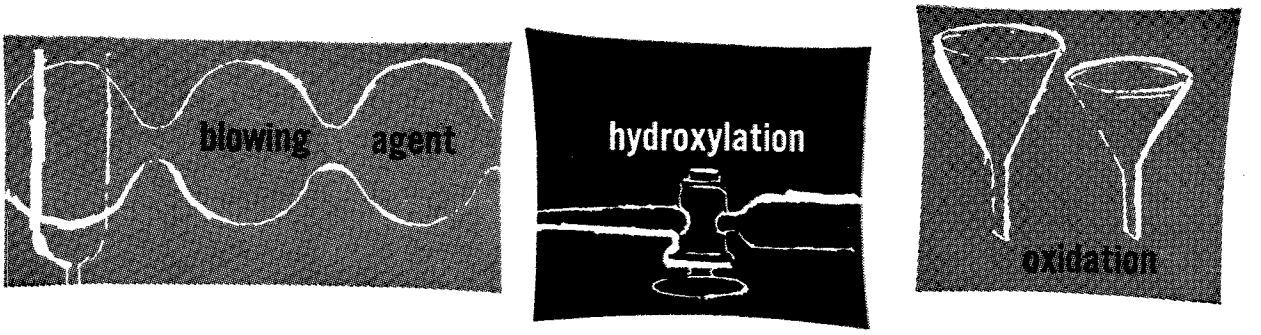
COATINGS AND POLYMERS cont.—W. O. Lundberg *(left end)* is chairman; the others are O. L. Brekke, H. P. Dupuy, and W. J. De Jarlais.

Acknowledgment

Appreciation is expressed to C. S. Nevin for covering the sessions on coatings and polymers and to P. A. Grasemann for covering sessions on soaps and syndets. Both are with the A. E. Staley Manufacturing Company.

S. S. Chang, A. E. Staley Manufacturing Company, Decatur, Ill.

LOOKING UP A REFERENCE—Antonio R. Pandolfi, of S. A. Moinhos Rio Grandenses, Porto Alegre, Brasil, consults Doris J. Kann, circulation manager of the Journal of the American Oil Chemists' Society, Chicago, in regard to the Cumulative 35-Year Index while at the 33rd fall meeting in Los Angeles.



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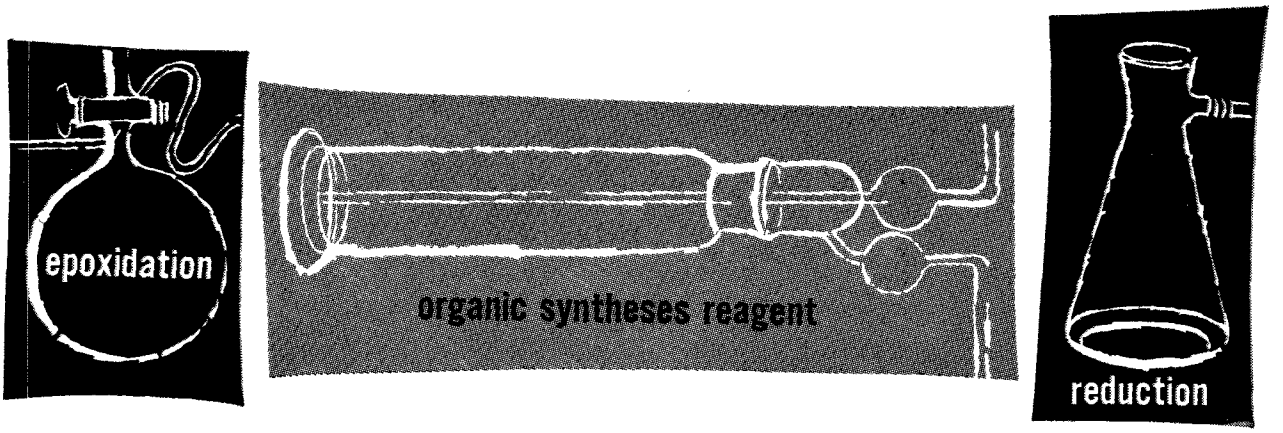

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