Report of Technical Sessions

Fall Meeting, Cincinnati, 1952

THIRTY-EIGHT scientific papers were presented at the three specialized and the two general sessions of the 26th fall meeting of the American Oil Chemists' Society, October 20-22, 1952, at Cincinnati's Netherland Plaza hotel.

The technical program opened with six papers on soaps and detergency.

Getty and McCready studied the viscosity and solubility of synthetic detergent mixtures containing soluble silicates and phosphates. Silicate pyrophosphate mixtures have lower viscosities and turbidities than silicate-tripolyphosphate mixtures. A mixture of the two phosphates with silicate results in a still lower viscosity but an intermediate turbidity.

In discussing foam stability, C. R. Sporck indicated that nonequilibrium film elasticity but not the equilibrium values may be responsible for foam stability.

Of particular interest to housewives would be the conclusion arrived at by Russell and Niven from a study of the relative merits of rinsing versus nonrinsing in home laundering. Using the newer type detergents, they report that non-rinse washing of lightly soiled family laundry can give satisfactory results at substantial savings in work time and cost.

In a discussion of whiteness it was pointed out by Hemmendinger and Lambert that of the three dimensions of color, lightness of artificially soiled, laundered cotton swatches has been used almost exclusively for the laboratory evaluation of detergents while the other two dimensions, hue and chroma, have been disregarded. From the experimental evidence obtained by using radioisotope-labeled synthetic soils, the investigators conclude that in objective laboratory evaluations of detergents, the influence of chromaticity (hue and chroma) on the appearance of the laundered cloth should be considered.

Knight, Koos, and Swern described a new method of preparing hydroxylated long-chain fatty acids, esters, alcohols, and hydrocarbons. Formic acid at its boiling point adds readily to the double bonds of unsaturated aliphatic compounds yielding the formate esters. Small amounts of perchloric acid reduce the reaction time from 24 hours to 5 to 15 minutes. The reaction goes best with nearly anhydrous formic acid. However the cheaper 85% to 90% formic acid can be used if glacial acetic acid or acetic anhydride are also added to take up the water. Oleic and elaidic acids were converted to monohydroxystearic acids, and linoleic acid yielded a mixture of monohydroxy and dihydroxy acids. Oleic alcohol gave a glycol and 1-hexane gave a mixture of 2- and 3-hexyl formates.

Barrett, Fitzpatrick, and Kadesh obtained sodium cyanate as a by-product of the production of fatty alcohols by reduction of triglycerides with sodium and alcohol. In the usual procedure quenching of the reaction mixture with water yields the fatty alcohol and an aqueous solution of glycerol and sodium hydroxide. By using urea instead of water to decompose the sodium alkoxides, valuable sodium cyanate precipitates and is filtered off. The yields of fatty alcohols are good, and glycerin is easily recovered.

FOUR papers were devoted to fatty acid-urea complexes. In the first of two papers Lloyd C. Fetterly told how the reversible, urea complex or "extractive crystallization" technique used with petroleum oils could be extended to fatty acids and esters. Two primary objectives were pursued: a) the separation of stearic and oleic acids and esters from the linoleic and linolenic components of drying oils and b) from this an explanation for semi-polar solvent influence and various inhibitory tendencies of urea-water mixtures. The latter was the subject of the second paper, in which the author said that an increase in the rate of complex formation of n-paraffin and fatty acids or methyl esters in methyl isobutyl ketone with urea solution was due to a decreased oil-water interfacial rate barrier and not to an equilibrium shift brought about by solubilization. The relative rate ratio of complex formation for oleic and linoleic acids showed a greater difference than their equilibrium ratio. As a result the non-equilibrium technique gave a better separation. For example, unsaturated soybean acids of iodine value 120 yielded a fraction with an iodine value of 175 as compared to the 154 iodine value of the equilibrium product.

Swern and Parker reported the preparation of oleic acid or methyl oleate concentrates from olive oil fatty acids or methyl esters by a single urea complex precipitation. The concentrates continued only about 1% of polyunsaturated contaminants, and one fractional distillation or crystallization yielded a product of 90-97% purity. Best results were obtained when the saturates were removed by fractional crystallization prior to a final distillation. In this way oleic acid and methyl oleate of high purity (97-99%) were obtained in 60-70% yields. Two techniques were used for the preparation of the urea complexes. With less than 1,000 g. of acids or esters a urea solution was used, but with large size experiments a slurry of urea in methanol was preferred. The latter method reduced considerably the volume of the mixture to be handled and gave somewhat higher yields in a shorter time. In a second paper by the same author Swern described the preparation of 85-95% linoleic concentrates in 50-70% yields from corn oil fatty acids and of 87-89% linolenic concentrates in 55-60% yields from perilla oil acids by preferential precipitation of the more saturated fatty acids with urea. Linseed oil fatty acids gave high yields (87-90%) of lower purity (66-70%) linolenic acid concentrates. A levelling-off effect was observed in the use of the preferential precipitation technique in raising the purity of linoleic and linolenic acid concentrates.

Carnauba wax fatty acids were found to contain 38% of normal acids, according to K. E. Murray. Amplified distillation revealed the presence of acids of even carbon number from C_{18} to C_{30}.

AUTOXIDATION SPEAKERS—From left to right *(first row)* these are H. J. Dutton, Ogden C. Johnson, S. T. Bauer, chairman, and S. S. Chang; *(second row)* C. D. Evans and N. A. Khan.

SOAP AND DETERGENCY—Speakers at this session were C. R. Sporck, Newton W. McCready, J. M. Lambert, Fred O. Barrett, and Mrs. Edith Russell. Procter Thomson *(right)* was chairman.

UREA COMPLEXES—Speakers on this topic and oil modification, with A. O. Snoddy as chairman, are shown above: J. S. Cromeans, Mr. Snoddy, P. O. Powers, and H. B. Knight; *(standing)* K. E. Murray, L. C. Fetterly, E. R. Cousins, R. O. Feuge, and Daniel Swern.

GENERAL TOPICS — Wednesday speakers included the above: *(first row)* R. W. Riemenschneider and Miles J. Willard Jr.; *(second row)* Duncan Macmillan, H. L. Craig, and H. J. Wissel; *(third row)* Wales Newby, R. C. Stillman, program chairman for the Cincinnati meeting, and D. F. Maskey.

R. O. Feuge and a group of researchers from the Southern Regional Research Laboratory presented two papers on modification of vegetable oils. In the first paper E. R. Cousins discussed the formation of isomers during hydrogenation of pure methyl linoleate in the presence of a nickel catalyst. Some conjugated linoleates were formed, and hydrogenation was necessary for their formation. No conjugation was formed as a result of heat and catalyst only. Elaidinization of linoleates took place to only a minor degree. Under given conditions the number of trans bonds formed appeared to be in direct proportion to the number of bonds hydrogenated. As hydrogenation proceeded beyond the disappearance of linoleates, the percentage of trans bonds did not come to an equilibrium of 67%, which was found to occur during hydrogenation of methyl oleate. Feuge then described the properties of aceto-oleins obtained by acetylating mono-olein. Such compounds have low melting points (—19°C.) and, when mixed with hydrogenated oils, impart to the mixture a large degree of plasticity over a wide temperature range. Tests performed during the past two years indicate that aceto-oleins are not toxic to laboratory animals.

J. S. Cromeans reviewed the development and use of industrial catalysts with particular emphasis on the hydrogenation catalysts.

THE Tuesday morning session was devoted exclusively to a symposium on autoxidation. Chang and Kummerow found that the polymers formed during autoxidation of ethyl linoleate as well as their hydrogenation products had a bitter rancid flavor and painty odor. The volatile products obtained by reautoxidation of the polymers were identified as n-pentanol and n-hexanol while the hydrogenated polymers yielded n-pentanol and 2-heptenal. Johnson, Chang, and Kummerow then described the isolation of 2-pentenal, acetaldehyde, and crotonaldehyde as volatile products from the reautoxidation of the polymers obtained by autoxidizing ethyl linolenate. It was suggested that the oxidative polymers from both ethyl linoleate and ethyl linolenate could serve as precursors of the compounds responsible for the reverted taste and odor of certain vegetable oils.

From ultraviolet and infrared absorption spectra and chemical analyses on hydroperoxide concentrates of methyl linoleate, O. S. Privett concluded that, at 0°C. and in the dark, oxidation of methyl linoleate yields mostly conjugated cis-trans hydroperoxides. Since previous estimates of the amount of conjugated peroxides formed during autoxidation have been based on the molecular extinction coefficient for conjugated trans, trans linoleic acid, and since cis, trans linoleic acid has a lower molecular extinction coefficient in the ultraviolet conjugated diene absorption region than its trans trans isomer, it is estimated that the hydroperoxides formed are at least 90% conjugated instead of the 70-75% conjugation reported previously. At higher temperatures (24°C.) appreciable amounts of conjugated trans-trans hydroperoxides were also present in addition to those of the cis trans type.

P. S. Hess reported on studies by Hess and O'Hare on bulk oxidation of the triglycerides of linolenic, linoleic, oleic, and stearic acid. Determination of changes in viscosity, dielectric constant, and power factor with respect to oxygen absorption and time to reach gelation indicate that bulk oxidations of trilinolein and trilinolenin are closely related while that of triolein is different. Tristearin is only slightly susceptible to oxidation. The behavior of linseed oil, soybean oil, and safflower oil in similar studies suggests that the presence of monoethenoid and saturated components in the natural oils effects a dilution of the active centers, keeping them sufficiently far apart and thereby increasing the possibilities with which the reactive portions of the molecule can add oxygen. Infra red measurements indicate that gelation is a physical reaction and not a chemical one. The similarities noted upon oxidizing trilinolein and trilinolenic are no longer true for heat polymerization. Trilinolenin reacts at a considerably faster rate than trilinolein or either of the natural oils.

According to N. A. Khan, autoxidation of deuterium-labelled oleate has furnished experimental evidence for a) an initial attack of oxygen at the double bond and the inherent induction period, b) the propagation of autoxidation by attack on methylenic groups alpha to the double bond, c) shifting of the double bond, and d) the location of the H atoms contributing to the formation of the major portion of the water. Water formation was shown to be the outcome of the primary decomposition of peroxides and the formation of the organic volatile products to be that of secondary decomposition at a later stage. These studies lend support to the theories of autoxidation proposed by Farmer.

Three papers from the Northern Regional Research Laboratory related flavor reversion to autoxidation. In two of these papers C. D. Evans discussed a number of nitrogen and sulfur compounds which can be used as metal deactivators to delay oxidation and flavor reversion of soybean oil. In discussing the present status of research on the flavor problem of soybean oil, Dutton integrated studies of odor precursors, autoxidation, trace metal deactivation, glyceride structure, odor isolations and identifications, and organoleptic procedures with the problem of flavor reversion.

ANALYTICAL procedures were the subject of seven papers. A paper by P. O. Powers and associates was devoted to a study of the factors influencing the determination of iodine values of unsaturated hydrocarbon resins. A large excess of reagent gives higher values which more nearly approximate the values expected from the unsaturation in the resin.

Herb and Riemenschneider described a microspectrophotometric method for determining polyunsaturated fatty acids. The tentative AOCS method CD-748 has been modified by using smaller reaction tubes, a higher alkali concentration (21% in glycol), and a shorter time (15 min.). New constants determined with natural polyunsaturated acids are used in the calculation. From 1 to 10 mg. sample is sufficient for analysis. If larger amounts of material are available, the use of lauryl alcohol as a diluent avoids the necessity of using a microbalance.

Three papers on measurement of color in oils are probably a reflection of the difficulties encountered two years ago when the oil from an immature soybean crop contained appreciable amounts of chlorophyll. Procter Thomson discussed some of the difficulties encountered when attempts are made to measure a three-dimensional quantity such as color by a single number system. Such a system assumes that the objects to be represented lie along a line in trichromatic space, and when a sample does not lie along this line, some compromise has to be made. The compromise that the Lovibond system makes when chlorophyll is present was described. Melvin, McMillan, and Senti correlated spectrophotometric measurements on green oils obtained from soybeans frozen at various stages of maturity. Both with the crude and refined oils good correlation was observed between optical densities and the depth of nickel sulfate solution required to match one inch of the oils, but there was poor correlation of the nickel sulfate readings on a crude oil with optical densities of the same oil after refining or bleaching. R. C. Stillman pointed out that as little as 1 p.p.m. of chlorophyll reduces the Lovibond color of an oil by about 2.6 units. Consequently, if insufficient amounts of bleaching earth are used, the color of the oil as measured is apparently darkened by bleaching due to removal of chlorophyll and not of the other pigments. These factors may lead to a misjudgment of the values of the oil and of the bleaching earth. Two papers by Ledbetter, Wissel, and Maskey and by Ledbetter, Maskey, and Craig described the development and application of dielectric type meters for the rapid and accurate determination of moisture in oil-bearing seed, and the subsequent development of a continuous moisture meter.

The only paper on fat metabolism was presented by Raymond Reiser. To two rats he fed 1-palmitoxy-3-hydroxy acetone labelled in both the fatty acid and dihydroxy acetone moieties with carbon 14. Measurement of the radioactivity in the glycerol and fatty acid fractions of lymph fat indicated that a large proportion of the dihydroxyacetone was converted to glycerol and appeared in the lymph fat.

KUBER and Newby found that the iodine values of acidulated coconut oil soapstock were consistently higher than that of the corresponding refined oil. These differences in iodine value were correlated with the free fatty acid content of the crude oils, suggesting that this may be due to a difference in the ease with which different chain length acids hydrolyze so that the free fatty acids present in the crude oil may differ from the combined acids.

N. A. Khan described the preparation of acetylenic compounds by dehydrobromination with sodamide in liquid ammonia. Selective hydrogenation of the acetylenic compounds yields monoolefinic substances free of traces of polyunsaturated constituents. Selective deuteration of the acetylenic acids or esters yields dideutero derivatives that may be employed as "tracers."

According to the paper by Cording, Willard, Edwards, and Eskew, the use of water-saturated solvents for the low temperature fractionation of white grease permits the use of crystallization temperature higher than that when anhydrous solvents are employed. The resulting saving in refrigeration costs however is accompanied by a lowering of yields. Joseph McLaughlin Jr. studied the ultraviolet absorption produced by alkali-isomerized fatty acids and showed that a straight line function was obtained when the square of the wavelength of the ultraviolet absorption maxima was plotted against the number of double bonds in the fatty acids.

The effect of variety and environment on the iodine value of cottonseed oil was studied by Stansbury, Hoffpauir, and Hopper. On the basis of eight varieties of cotton grown in 13 locations over a period of three years the results indicated highly significant differences in iodine values, due to both variety and temperatures prevailing during the periods of growth and maturation. The iodine value was negatively correlated with the temperature, and more significantly so for the period of maturation when the oil was being synthesized. Application of the filtration-extraction process to rice bran in pilot-plant equipment was described by J. J. Spadaro.

D. F. Maskey discussed the effect of mineral oil contamination on the color and fluorescence of vegetable oils.

Drying oils prepared by esterification of methyl alpha-D-glucoside with linseed oil fatty acids were described by Gibbons and Janke. These oils possessed more rapid bodying characteristics at 310° than similarly prepared glycerol or pentaerythritol oils. They may be used with Bakelite resin to give varnishes that dry quickly to hard films with good alkali and water resistance and excellent adhesive properties.

AT the business meeting of the Society on October 22, 1952, several decisions were made affecting the Official and Tentative Methods of the Society. Minor revisions were made in Official Methods Cc-13b and Cc-13c for the determination of color in oils. Upon the recommendation of the Refining Committee, minor changes were also made in the bleaching tests, Official Methods Cc-8a and Cc-8b. In particular, allowance was made for the cooling of samples either in a water or air bath.

Changes were also made in methods applicable to tung fruit, seed, meal, and oil. In method Ad-1-48 the method of sampling was revised and the method continued as tentative. Method Ad-2-48 for determining moisture and volatile matter was revised to include hulls and tung fruit and the method was changed from tentative to official. Methods Ad-3-48, 4-48, and 5-48 for the determination of tung oil in fruit, kernels, etc., were given official status. A new method was proposed for the analysis of oil in hulls and tung fruit and was adopted as tentative.

Several proposals concerning analyses applicable to castor beans and products were also adopted.

An important action affecting a number of the Society's analytical procedures was the adoption of specifications for the standardization of solutions of H_2SO_4, HCl, NaOH, and alcoholic KOH. It was decided that the standardization of such solutions should be based on the use of a standard potassium acid phthalate obtained from the Bureau of Standards.

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