ABSTRACTS OF PAPERS 55TH ANNUAL MEETING NEW ORLEANS, LA.

— 1 —

EFFECT OF SOME UNUSUAL ACIDS ON SELECTED SEED OIL ANALYSES

I. A. Wolff

Seeds from over 2600 species of uncultivated plants collected from worldwide sources have been given exploratory chemical analyses to permit choosing for more intensive study any that have potential as new oilseed crops. From studies with such a large and diverse group of seed oils many observations have been made on unexcepted responses, given to frequently used analytical procedures, that were not readily explainable by available knowledge. Investigation of the oils that gave such results led to the discovery and structural characterization of a dozen new fatty acids and also led to finding new sources of known acids of limited distribution. Examples will be reviewed to illustrate results encountered from use of selected methods, to comment on the explanations developed, and to discuss procedures found useful in surveying a wide variety of oils. Included will be remarks on exploratory hydrogenation studies on oils by T. K. Miwa of this laboratory, for which he has used the automatic titration procedure recently developed by Brown and Brown at Purdue University.

— 2 —

A REVIEW OF ANTIOXIDANT ANALYSIS IN FOOD PRODUCTS

B. N. Stuckey and C. E. Osborne

To permit proper usage of antioxidants by the food processor and permit control under applicable governmental regulations, it is necessary to have adequate analytical methods. Such methods should both positively identify and provide a quantitative assay for the additive. Due to the complex nature of foods, analysis of an antioxidant in the very small quantities used presents a very real problem. Solvent extraction and/or steam distillation techniques are employed to separate the antioxidants from the food. Slight variations are necessary for each type of food. The separated antioxidant must then be identified and the amount present be determined. Three methods are used:

1) Ultraviolet Spectra: UV measurements are applicable only to relatively pure extracts containing only one or two antioxidants because of interfering substances extracted from the foods. However, column chromatography can sometimes be used to remove the interference.

2) Colorimetric Measurements: Reaction of the antioxidant with a reagent to form a colored compound which can be measured quantitatively is currently the most widely used analytical technique. This method suffers, however, from some lack of specificity and from some interferences by materials extracted from the foods.

3) Gas Chromatographic Methods: Gas chromatography has received attention in the last few years for analysis of BHA and BHT in foods. Published data describe the use of the extremely sensitive flame ionization detection system for analysis of solvent extracts. However, the extreme sensitivity of the method can result in interference from the "bleed" of the column packing. A method utilizing the much less sensitive thermal conductivity detection system has been developed. This requires the use of a large sample of extract in order to have a measurable amount of BHA and BHT. However, there is no problem with bleeding column packing. Several column packings have been developed to solve problems of interference of other materials extracted from the food.

— 3 —

QUANTITATIVE DETERMINATION OF PHOSPHOLIPIDS AND POLAR LIPIDS IN THE PRESENCE OF LARGE AMOUNTS OF NEUTRAL LIPIDS

George Rouser, Dorothy Heller, and Thomas Bernat

The determination of the individual polar lipid classes in the presence of large amounts of neutral lipid presents special problems. Three general methods will be considered: column chromatography, thin layer chromatography, (TLC) and a combination of column and TLC. Column chromatography on silicic acid, magnesim silicate, and diethylaminoethyl (DEAE) cellulose columns; TLC using adsorbents composed of silicic acid and calcium sulfate or silicic acid with magnesium silicate; and a combination of column chromatography with TLC using the sulfuric acid-potassium dichromate spray reagent followed by quantitative densitometric determination of the extent of charring will be described. Column chromatographic procedures can be utilized to isolate adequate quantities of even very small amounts of polar lipids in the presence of very large amounts of neutral lipids while the quantitative TLC procedure offers a rapid, simple, and reasonably accurate method for the determination of polar lipids in the presence of large amounts of nonpolar lipids using small samples. A combination of column and quantitative TLC is of special value because the overlap of polar lipid components observed with one dimensional chromatography can be prevented to a great extent by the proper type of column chromatography, while quantitative TLC is rapid and small samples can be used.

— 4 —

THE DETERGENTS AND WATER QUALITY STANDARDS

L. W. Weinberger and T. J. Powers

In 1961, Congress gave the Secretary of Health, Education, and Welfare the responsibility of determining the effects of pollutants on all water uses.

Two new water quality laboratories are being built. One is for fresh water research, the other for salt water. From this research on effects will come water quality standards related to water use. The 600 million lb/year of detergents reaching the water environment from households alone represents an important area for study. All of the detergents in common use will be examined.

The Federal research program also includes work on new methods to effectively remove detergents from water. Some of the newer methods are ready for field evaluation. Close cooperation with the industry will be maintained.

— 5 —

DETERGENT DEVELOPMENTS TO PROTECT WATER QUALITY

C. G. Bueltman and E. S. Pattison

In a little more than a decade we have witnessed a cycle of awareness of, investigation into, research for an answer, and finally the solution of the problem popularly called "detergent pollution." The ebb and flow of public awareness and opinion paralleling the steady progress of technological advance is an interesting case history.

Starting in the late-1940's-early-1950's the sanitary engineering profession recognized an increase in amount and persistence of foaming on sewage treatment plants. Immediate allegations that detergent residues grossly upset and interfered with sewage treatment slowly gave way, under the wt of scientific investigation, to the understanding that detergent residues created a maintenance problem, but in no other way interfered with sewage treatment operations. Further study pointed out the possible constructive use of detergent residues in tertiary treatment and advanced waste treatment processes.

The same cycle of concern and final realizaion of the minor, if any at all, contribution that detergent residues made to public health, wild life, water resource degradation, and aquatic life problems has been essentially completed thoughout the technical and scientific community. The final conclusion: detergent residues do pose an esthetic problem, but in no instance do they pose a threat to public health and welfare.

We are now at the pinnacle of concern on the part of the general and lay public. To them, foam on the surface of water immediately signifies detergent residues, with the deduction that detergent residues cause the gross pollution rather than being a minor portion of the total pollution. Legislators have reflected public opinion through the introduction of anti-detergent legislation in several states and at the federal level. A review of the nature of the legislation, and the supporting arguments for it, indicates the extent of public knowledge concerning gross pollution and the true nature of the overall problem.

The soap and detergent industry assumed the responsibility for correcting its minor contribution to pollution problems. Many years of intensive research is culminating in a dramatic technological change in the industry, permitting a complete change-over to household detergents with a surfactant base designed to alleviate foaming incidences due to detergents residues, maintaining or exceeding present product functional performance by December 31, 1965.

— 6 —

MEASUREMENT OF BIODEGRADABILITY

P. J. Weaver and F. J. Coughlin

Methods which have been used in evaluating biodegradability of various types of surface-active agents, including the procedure adopted in the German regulations, will be described. To the extent possible, attempts will be made to correlate laboratory tests and practical experience.

— 7 —

FISH BIOASSAYS OF STRAIGHT CHAIN ABS SURFACTANTS AND INTERMEDIATE DEGRADATION PRODUCTS

R. D. Swisher, J. T. O'Rourke and H. D. Tomlinson

Straight chain alkylbenzene sulfonates (ABS) are relatively toxic to fish when tested under static conditions by standard bioassay techinques, the mean tolerance limit (TL_m) being ca. 3 mg/liter and 0.6 mg/liter for the C_{12} and C_{14} homologs, respectively. However, these materials are so readily degraded by bacterial attack that bluegill fingerlings live with no trouble in effluents from laboratory continuous flow activated sludge units being fed 100 mg/liter or more of either product. No effects on the fish were noticeable in exposures of 96 hr or more, except for slight alterations in the microscopic appearance of the gill tissue. Thus, the removal of the ABS by biodegradation is paralleled by the removal of toxicity and there is no indication that toxic intermediates accumulate during the biodegradation process. This conclusion is substantiated by the observation of a much lower degree of toxicity (TL_m 75 mg/liter) for sulfophenylundecanoic acid disodium salt (mixed isomers), synthesized as a model of an intermediate degradation product.

— 8 —

CHEMICAL REQUIREMENTS OF THE MEAT INSPECTION DIVISION, AGRICULTURAL RESEARCH SERVICE, U.S. DEPARTMENT OF AGRICULTURE, AS THEY APPLY TO THE FAT AND OIL INDUSTRY

O. L. Bennett

This paper briefly describes the organization and functions of the Chemical Evaluation and Control Office of the Meat Inspection Division. Portions of the Meat Inspection Act, giving authority for the control of chemicals, are cited. It defines the extent of coverage, procedures for determining compliance, criteria used in evaluating safety or suitability of chemicals used in the treatment of fats and fat derivatives used in meat food products. Requirements covering the use of detergents, paints, adhesives, packaging materials, insecticides and other miscellaneous substances used in the packing plant are discussed. System of checking employed by field laboratories and in-plant inspectors is mentioned. Contact points with representatives of Division are noted. Publications such as the Regulations, MID memoranda, Manual of Inspection Procedures or other pamphlets available for distribution which provide information on various phases of control of additives or products are discussed.

— 9 —

AUTOMATED MANOMETRIC APPARATUS

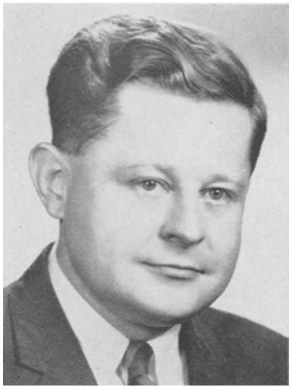
E. D. Bitner and H. J. Dutton

Automatic manometric appartus has been developed for performing hydrogenations, autoxidations, and similar gas-liquid phase reactions.

Biodegradable Detergents Symposium Feature of New Orleans Meeting

Eric Jungermann, chairman of the AOCS Symposium of Biodegradable Detergents, announced completion of the program scheduled for Monday, April 20, 1964, as part of the Annual Spring Meeting in New Orleans.

The scope and timing of the symposium re-emphasizes the interest of the AOCS in this area of technology and science and promises to be one of the highlights of the Spring Session.



Eric Jungermann

Due to the great interest generated by the Symposium, there will be both a morning and afternoon session. "We were particularly fortunate," Dr. Jungermann stated, "in being able to bring together representatives of government and all segments of industry."

The morning session will be devoted to the general problems of biodegradability. Current government approach will be presented by L. W. Weinberger and T. P. Towers, Department of Health, Education and Welfare, Washington, who will discuss the topic of "Detergents and Water Quality Standards." A representative from the Soap and Detergent Association will discuss "Detergent Pollution as a Public Issue." The tremendous progress made by all of the industry toward achieving the anticipated switch to biodegradable detergents by December 1965 will be detailed. P. J. Weaver and F. J. Coughlin, The Procter & Gamble Co., will discuss "The Measurement of Biodegradability," describing various methods used in evaluating biodegradability, including a discussion of regulations enacted into law in Germany. Whenever possible, the authors will attempt to correlate laboratory tests with practical experience. The last paper of the morning session will be presented by R. D. Swisher, Monsanto Chemical Co., and will deal with some very recent data on the toxicity of straight chain alkylbenzenes and their degradation products. His talk is entitled "Fish Bioassay of Straight Chain ABS and Intermediate Biodegradation Products."

The afternoon session will deal with more specific aspects of the new biodegradable detergents, their chemistry, properites and evaluation methodology. Two papers will be presented on evaluation techniques: R. L. Huddleston and R. C. Allred, Continental Oil Co., will discuss "The Evaluation of Detergent Biodegradation Using Activated Sludge," while L. J. Garrison and R. D. Matson, Jefferson Chemical Co., will compare the results obtained using different testing techniques with selected nonionic surface-active agents. Also part of the afternoon session are three papers dealing with a correlation of structural modification of new biodegradable surface-active molecules with their performance characteristics. B. C. Steinle, R. C. Myerle, and C. A. Bass from Union Carbide Chemical Co., will discuss "Surfactants Containing Ethylene Oxide: Relationship of Structure to Biodegradability." This will be followed by J. H. McFarland and P. R. Kinkel discussing the performance and physical properties of biogradable surfactants prepared from straight chain secondary alcohols. Another paper by W. A. Sweeney, California Research Corp., will discuss "Performance Characteristics of Straight Chain Alkylbenzene Sulfonates." The last talk of this session will be presented by C. A. Brunner of the Advanced Waste Treatment Research DHEW, R. A. Taft Engineering Center of Cincinnati, Ohio, who will discuss "Methods for Removing Detergents from Waste Water."

The session will conclude with a panel discussion. All members of the Symposium will participate and Dr. Jungermann will act as moderator. Questions from the audience will be welcome. Full details of the complete Technical Program and abstracts of papers start on page 4.

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Incorporation of an ion chamber permits radioactive isotope experiments. Nonradioactive isotopes (such as deuterium and O^{18}) are monitored by attaching the apparatus to a mass spectrometer. Automatic recording of gas volume and radioactivity establishes a permanent record and allows unattended operation. Use of a servo-motor driven syringe eliminates all mercury, including mercury leveling bulbs. The flow-through construction of the syringe permits circulation of the gas phase and obviates, as required in isotopic experiments, the dead space inherent in classical manometers. Simplified electronics and readily available components enhance operation and construction. Typical hydrogenations with accompanying graphs showing gas uptake, reaction time, and radioactivity concn illustrate the utility of the apparatus and the ease with which data are obtained.

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QUANTITATIVE MEASURE OF THE SELECTIVITY OF HYDROGENATION OF TRIGLYCERIDES

L. F. Albright

Graphs have been prepared which are useful in quantitatively determining the degree of selectivity for hydrogenation of cottonseed, corn, peanut, soybean, and linseed oils. Use of these graphs requires a knowledge only of the compositions of the initial (unhydrogenated) and of the final (hydrogenated) oils. In most cases, a typical composition can be assumed for the initial oil if the specific composition is unknown.

The graphs were prepared using analytical equations similar to those initially proposed by Bailey. The various unsaturated fatty acid groups are assumed to hydrogenate in an irreversible first-order manner. This model has been found by several investigators to give a good fit of experimental data. The equations (involving reaction rate constants for linoleic, oleic, and other unsaturated acid groups) were programmed and solved on an IBM 7090 digital computer. The selectivity ratio defined as the ratio of the rate constant for the linoleic acid group divided by that for the oleic acid group can be easily determined from the graphs.

— 11 —

EFFECT OF RE-USED NICKEL CATALYST ON THE HYDROGENATION OF COTTONSEED OIL

L. F. Albright, M. M. Win and J. M. Woods

Refined and bleached cottonseed oil was hydrogenated in a dead-end reactor using both new (Rufert catalyst flakes) and reused (up to 5 uses) catalyst at a concn of 0.10% nickel (by wt). Hydrogenation runs were made at temp from 130–169C, at a pressure of 45 psig, and with sufficient agitation to minimize resistances of mass transfer of the reactants to the catalyst surface.

A comparison of the hydrogenation results for runs with new and re-used catalysts indicate the following effects:

1) The activity of the catalyst increased initially with use, but with continued use the activity decreased. This effect was especially pronounced at 130C where third-use catalyst resulted in the most rapid rate of hydrogenation.

2) Selectivity and isomerization changed somewhat as the catalyst was re-used. Selectivity, especially at 130C, decreased with re-use of the catalyst. At 130C, isomerization was not significantly affected with catalyst re-use, but at 169C, however, it decreased slightly.

3) The induction period found with fresh catalyst at 130C was eliminated in runs with second- and third-use catalyst. A small induction period was noted with fifth-use catalyst.

Once-use catalyst was treated in a series of runs in different manners. Air-treatment severely reduced the catalyst activity. Steam- and vacuum-treatment of the catalyst resulted in a slightly less active catalyst than a comparable run in which the catalyst was maintained for a longer period of time in a hydrogen atmosphere. None of these treatments significantly affected the selectivity or isomerization of the subsequent run.

Results of this investigation can be explained in large part by the concn of hydrogen adsorbed on the catalyst surface.

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A COMPARISON OF ALCOHOLS AS PARTICIPATING SOLVENTS DURING OZONIZATION

D. J. Moore, E. H. Pryde and J. C. Cowan

According to the Criegee mechanism for ozonization of olefins, a zwitterion intermediate can competitively react with itself, with carbonyl compounds, or with a participating solvent. Of the solvents reported, apparently only methanol gives exclusive formation of alkoxy hydroperoxides to permit a high yield of aldehyde upon reduction; however, methanol has certain disadvantages, including volatility and poor solvent properties. Accordingly, we undertook a search for a participating solvent more generally useful. With ionization constants as a guide to nucleophilic properties, a number of solvents were selected for testing: 2-methoxyethyl, 2-(2-methoxyethoxy)ethyl, and benzyl alcohols; ethylene and diethylene glycols; and α-hydroxyethyl acetate. Both chemical and catalytic reduction were investigated along with volatility, solubility, ozone uptake, by-product formation, and total carbonyl yield.

Carbonyl yields for chemically reduced samples were 80–96%; those with benzyl alcohol and 2-methoxyethanol were comparable to those with methanol. Yields by catalytic reduction (10% Pd/C or Lindlar catalysts) were 75–85%. Side reactions with catalytic reduction gave the esters expected as well as free acids. When pyridine was used with 10% Pd/C and 2-methoxyethanol, the yield of carbonyl was less than 70% and free acids were formed, in contrast to the higher yields reported with pyridine in methanol. The difference suggests that a neighboring group, the ether oxygen, is participating in decomposition of the hydroperoxides.

With the solvents tested, volatility losses were low and ozone uptake was about the same as that for methanol. The heterogeneity of the reaction medium probably accounts for the poorer yields of aldehydes with both glycols and α-hydroxyethyl acetate.

— 13 —

POLYMORPHIC BEHAVIOR OF OLEODISTEARINS AND THEIR MIXTURES

N. V. Lovegren, R. O. Feuge and Werner Landmann

2-Oleodistearin (SOS), 1-oleodistearin (OSS), and their mixtures were examined dilatometrically and by X-ray diffraction. The various polymorphic forms and rates of conversion of one form to another were determined and investigated.

Mixtures of SOS and OSS containing 75% and 50% SOS melted like mixtures of two compounds, each of which is not very soluble in the other. The mixture containing 25% SOS behaved like a single compound. This mixture has an unexpected intermediate melting polymorph whose X-ray pattern is not characteristic of pure SOS or OSS.

Mixing one compound with the other tends to stabilize the lower melting polymorphs and make them more resistant to change over short intervals of time. However, on tempering these mixtures for 1.5 weeks the transformation of the difficult-to-temper SOS to its highest melting polymorph was faster than the rate of transformation of the pure SOS. Contrary to heretofore accepted opinion, the tempering of a triglyceride probably can be facilitated by the presence of certain other triglycerides as impurities.

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SPECIFIC ORIENTATION IN FAT MOLECULES

R. J. VanderWal, H. J. Ast, E. G. Perkins and G. K. Chacko

It is well known that in the natural fats the component fatty acids show varying specificities for the 2- or 1,3- position of the fat molecules. Specificities, when defined as per cent of positive deviation from random values, can be expressed in mathematical terms independent of concn. The specificities so calculated of the component acids in various natural fats are recorded. Some biological significance of the data is discussed.

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THE PHOSPHOLIPIDS OF AUTOLOGOUS NORMAL HUMAN ERYTHROCYTES AND LEUKOCYTES

K. Arai, R. M. Fritz, W. C. Levin and S. R. Brown

Analyses of the phospholipids of autologous normal human erythrocytes and leukocytes have been performed on freshly obtained, unstored blood. Following separation and washing of the erythrocytes and leukocytes, the lipids were extracted as Folch extracts, which were analyzed by well-known chromatographic techniques. By TLC the phospholipids were separated into fractions: 1) a mixture of serine and inositol phosphoglycerides, sphingomyelin and traces of lyso- compounds; 2) choline phosphoglycerides; 3) ethanolamine phosphoglycerides; and 4) polyglycerolphosphatides and phosphatidic acid. These fractions have been characterized by silicic acid paper and glass fiber filter paper chromatography, phosphorus content, ninhydrin reaction, and iodine titration. On the basis of distribution of lipid phosphorus, it has been demonstrated that in the normal individual, the ethanolamine phosphoglycerides constitute 26–30% of both erythrocyte and leukocyte phospholipids, whereas the choline phosphoglycerides are richer in leukocytes, comprising 43–49% in these cells as compared with 36–40% in erythrocytes. Fraction 1 contains 20–25% of the leukocyte and 30–34% of the erythrocyte lipid phosphorus. GLC analyses of the acyl and aldehydogenic groups of fractions 2 and 3 have been performed, and the characteristic differences will be presented.

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CHROMATOGRAPHICALLY HOMOGENEOUS LECITHIN FROM EGG PHOSPHOLIPIDS

W. S. Singleton, M. S. Gray, M. L. Brown and J. L. White

Lecithin has been isolated from crude egg phosphatides by column chromatography on alumina through modification of existing, lengthy methods. The isolated lecithin was chromatographically homogeneous, as determined by TLC on Silica Gel G. The crude egg phosphatides were applied to the chromatographic column in the ratio of 1 g phosphatides/25 g alumina, which proportion was required for effective resolution of the homogeneous lecithin from impurities, and avoidance of overloading of the column. A two-component solvent system, cholorform:methanol, 9:1 by volume, was used for elution of the lecithin. Use of the same solvents at a ratio of 1:1, by volume, or use of 95% ethanol, eluted a lecithin fraction which was contaminated with lysophosphatides. The modifications described have made unnecessary the need for a second chromatographic separation of egg lecithin on silicic acid, required in existing purification methods for the removal of lysophosphatides from alumina-chromatographed lecithin. The use of fresh yolks permitted easier removal of pigment from the final product than did dried yolks.

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CHROMATOGRAPHICALLY HOMOGENEOUS EGG LECITHIN AS STABILIZER OF EMULSIONS FOR INTRAVENOUS NUTRITION

H. J. Zeringue, M. L. Brown and W. S. Singleton

Physically stable emulsions of cottonseed and soybean oils have been prepared with chromatographically homogeneous lecithin from egg yolks as the sole emulsifier. These emulsions, which were developed for possible use in intravenous nutrition, consisted of either of the above oils at 20% concn, 1% of the lecithin emulsifier, and an isotonic aqueous phase. The physical stability of the lecithin stabilized emulsions was determined to be a direct function of pH, which must be adjusted to an optimum value of 6.8, and there must be no significant decrease in this value upon autoclaving at 121C for 15 min. Emulsions with an isotonic solution of glycerol as the aqueous phase conformed to the above conditions, whereas emulsions with isotonic solutions of dextrose as the aqueous phas decreased in pH to 4.9, and the emulsion invariably exhibited phase separation upon autoclaving. The cause of phase separation in the latter emulsion was due not to a change of emulsifying efficiency of the lecithin component, but to a change in the pH of the emulsion system as influenced by the dextrose solution which comprised the aqueous phase.

The sizes of the dispersed fat particles of the lecithin-stabilized emulsions and the distribution of these sizes were determined by the Coulter Counter.

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THE EFFECT OF n-OCTADECYL NITRATE ON THE FATTY ACID COMPOSITION OF THE ORGANS IN THE RAT

C. R. Houle, D. C. Malins and Louis Pegus

Despite an abundance of data on the physiological effects of short-chain nitrate esters (e.g., amyl nitrate), little is known of the physiological properties or metabolic fate of their long-chain homologues. This paper reports some effects on the organ wt and lipid composition of rats fed a diet containing *n*-octadecyl nitrate.

Five matching groups of weanling male rats were placed on purified diets containing either 5% saturated long-chain triglycerides from coconut oil or 4% saturated long-chain triglycerides from coconut oil and 1% *n*-octadecyl nitrate. The epididymal tissue, kindey, liver, heart, and serum of each animal were recovered for studies on the composition of the lipids after holding the animals on the experimental and control diets for 40 days.

Thin-layer chromatography (TLC) of the total lipid from the epididymal tissue, kidney, liver, and heart of each group showed 0.1–0.3% residual *n*-octadecyl nitrate in the epididymal tissue, 0.1% in the kidney, but no detectable amount in the liver and heart. GLC of methyl esters derived from the total lipids indicated that the greatest differences between the control and experimental groups were in the fatty acids of the depot fat and kidney. In the depot fat of the experimental rats, lauric, myristic, and myristoleic acid concn were lower than in the controls. Stearic and oleic acid concn, however, showed marked increases. The increase in oleic acid was particularly striking: it averaged 42.2% of the total in the rats fed *n*-octadecyl nitrate, compared to an average of 31.7% in the controls. The heart lipids of the experimental rats showed decreases in the amounts of palmitoleic, oleic, and docosenoic acids. These changes in the heart lipids were accompanied by a significant increase in the concn of linoleic acid in that organ.

Although the rats fed *n*-octadecyl nitrate appeared normal, their organ and body wt were generally lower than the controls. In addition, the fatty acid composition in these animals was significantly modified despite the fact that only traces of *n*-octadecyl nitrate could be detected in their organs.

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ACTIVATION AND SPECIFICITY OF CRAMBE ABYSSINICA SEED LIPASE

H. L. Tookey

The stability of oil in the seed of *Crambe abyssinica* was studied at various moisture levels; the seed was crushed to accelerate the effect of the lipase present. The lipase of crambe seed is inactive at 5–7% moisture at room temp. Lipase activity is very low even at 10–15% moisture; free acids in the crambe oil increase 1.6% to a total of 4% in 6 weeks. At higher moisture levels the lipase is active, hydrolyzing the oil in 5–7 weeks. These results indicate good stability of the oil during the usual steps in seed processing.

Crambe lipase hydrolyzes triglycerides in a nearly random fashion. The hydrolysis pattern indicates a small preference for the shorter chain acids (C_{16} and C_{18}), but no specificity for position in the triglyceride is apparent.

— 20 —

ANALYSIS OF CYCLOPROPANOID AND CYCLOPROPENOID ACID IN FATS AND OILS

F. C. Magne

The analysis of cyclopropenoid acids may be considered, from a historical standpoint, to have started with the discovery of the Halphen Test. Although this test as originally conceived was utilized as a means of detecting adulteration of premium edible oils with cottonseed oil, it has since been shown to be a characteristic test for cyclopropenoid fatty acids and has been adapted with various modifications as a quantitative colorimetric test for these substances. More recently, spectrophotometric methods particularly in the IR region have been applied to the analysis of these substances. The 9.8 μ band, characteristics of the cyclopropane, and the 9.91 μ band, characteristic of the cyclopropene group, as well as the 11.0 μ band, characteristic of some of the noncyclic degradation derivatives, have been utilized. GLC has been applied to the methyl esters of cyclopropanoid and hydrogenated cyclopropenoid acids. The reactivity of the cyclopropene ring toward hydrohalogens has been the basis of several analytical methods developed for use with cyclopropene acid-containing oils. Both aqueous and nonaqueous solutions of hydrohalogens have been employed.

These and other potential methods and approaches will be discussed and intercompared both as to their advantages and limitations.

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ANALYSIS OF POSITIONAL FATTY ACID ISOMERS

R. A. Stein

The chemical degradation or alteration step in the sequences of acts that is necessarily performed to distinguish between structurally similar unsaturated fatty acids is discussed. Olefin, substituted olefin and acetylene systems are considered with respect to their reactions, products and product analyses.

— 22 —

ANALYTICAL TECHNIQUES FOR HYDROXY ACIDS IN FATS AND OILS

T. H. Applewhite

Hydroxy fatty acids are an interesting class of compounds occurring in numerous fats and oils. The alcohol moiety alone or in conjunction with other functional groups presents challenging separation, charac-

(Continued on page 20)

(Continued from page 16)

terization, and quantitization problems. Recent work on separation techniques such as column, thin-layer, gas-liquid, and liquid-liquid partition chromatography; chemical and physical characterization techniques, e.g., derivatization, X-ray, IR, nuclear magnetic, and mass spectrographic methods; and the possibilities for qualitative and quantitative analysis using these and other methods will be discussed.

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DETERMINATION OF OXIRANE CONTENT OF DERIVATIVES OF FATS

G. Maerker

The epoxide ring is a functional group which reacts readily with a large variety of chemical reagents. Accordingly many different methods to analyze compounds for their oxirane content have been devised.

To date, however, no single analytical method has been universally successful in measuring the oxirane content of all compounds. This failure is ascribable to the great reactivity of the three-membered cyclic group and to the manner in which this reactivity is modified by molecular structure and by the presence of nearby substituents.

A survey of the various types of published analytical methods will be given, but major emphasis will be placed upon a discussion of procedures applicable to the analysis of epoxy derivatives of fats. Most of these latter methods depend upon the addition of some reagent, HX, to the epoxide ring with simultaneous cleavage of a carbon-oxygen bond. Side reactions and interfering substances will be pointed out.

— 24 —

A REVIEW OF METHODS AND TECHNIQUES FOR ANALYSIS OF LIPIDS AND RELATED PEROXIDES

L. S. Silbert

The major, general methods of organic peroxide analyses that include iodometric methods, metallo-reductions by ferrous ion, stannous ion and arsenious oxide methods, hydrogenation, oxidation, chromatography including paper, column, thin-layer and GLC variations, colorimetry and instrumental techniques such as potentiometric, IR and polarographic methods are reviewed. These general techniques have been applied to the detection, isolation and quantitative determination of lipid peroxides. Analyses of ozonides are included in this survey. Inadequacies and criticisms of some of the methods coupled with suggestions for future studies required for developing reliable and convenient techniques are presented.

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EVALUATION OF DETERGENT DEGRADATION USING ACTIVATED SLUDGE

R. L. Huddleston and R. C. Allred

Continuous feed activated sludge systems provide excellent facilities for evaluating detergent biodegradability only when the environmental conditions can be rigidly controlled. Degradation is rapid in such a system and because of the microbial culture used, the rate and extent should closely approximate detergent decomposition in many municipal waste disposal plants. The design, operation of, and detergent degradation patterns obtained from such a continuous feed activated sludge unit are described.

— 26 —

A COMPARISON BY WARBURG RESPIROMETRY AND DIE-AWAY STUDIES OF THE DEGRADABILITY OF SELECT NONIONIC SURFACE-ACTIVE AGENTS

L. J. Garrison and R. D. Matson

Much has been said and written recently concerning the measurement and identification of anionic surfactants after exposure to oxidative influences.

Work on nonionic products has been less extensively performed and reported due to the lesser volumes used in synthetic detergent products. Since there has been no established, accurate, direct analytical procedure for the detection of nonionic products, degradation studies involved oxygen uptake studies or measurement of loss of surfactancy properties (foamability or surface tension) by various die-away test procedures.

This paper reports an investigation and possible correlation of relative degradability of several of the commercially significant alkylene oxide nonionic structures using results of Warburg Respirometer and Die-Away Studies. Comparative data are presented on one commercially available alkylbenzene sulfonate.

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SURFACTANTS CONTAINING ETHYLENE OXIDE: RELATIONSHIP OF STRUCTURE TO BIODEGRADABILITY

E. C. Steinle, R. C. Myerly and C. A. Vath

Commercially-feasible biodegradable surfactants of the anionic and nonionic classes are prepared from straight-chain hydrocarbon precursors by the addition of water-solubilizing groups to functional links such as hydroxyl or aromatic groups. Surfactant families of major importance may be derived from the following straight-chain hydrophobes: fatty or Ziegler primary alcohol, OXO alcohols derived from straight-chain olefins, secondary straight-chain alcohols recently introduced by Union Carbide Corp., straight-chain alkylphenols and straight-chain alkylbenzenes.

Anionic sulfate, ethoxy sulfate, and nonionic ethoxylate surfactants prepared from the above hydrophobes have been studied in an effort to relate biodegradability to the following elements of structure: the nature of the connecting link, its position of attachment to the straight-chain hydrophobe, the chain length of the hydrophobe, and the length of the ethylene oxide chain used. Biodegradation in river water as well as activated sludge and other environments was estimated by known methods to show both rate of disappearance of surfactant as well as completeness of degradation.

Data are presented to support the following conclusions:

1) All surfactants derived from straight-chain primary and secondary alcohols are rapidly and completely degraded with loss of surfactant properties. The length of the ethylene oxide chain from zero up to 10 units has no effect on the rate or the completeness of degradation. In such surfactants, the ethylene oxide chain is completely degraded.

2) In contrast, surfactants from straight-chain alkylphenols are not as rapidly or as completely degraded as those described above. The position of attachment of the phenol ring to the straight chain has a large effect on degradability; normal or primary attachment leads to a faster rate of disappearance than secondary attachment. Nonionic surfactants from straight-chain alkylphenols containing 10–12 moles ethylene oxide are not completely degradable.

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DISCUSSION OF PERFORMANCE AND PHYSICAL PROPERTIES OF BIODEGRADABLE SURFACTANTS PREPARED FROM THE STRAIGHT CHAIN SECONDARY ALCOHOLS

J. H. McFarland and P. R. Kinkel

Surfactants based on the straight chain secondary alcohols provide a new source of biodegradable detergents. The nonionic and ethoxy sulfate derivatives of the alcohols are discussed in relationship to their physical properties and performance in detergent formulations. The physical properties presented are solubility, viscosity, surface tension, wetting, and lime soap dispersing ability. The performance properties of these derivatives in heavy-duty and light-duty liquid detergent formulations are defined by the results of detergency and foam stability tests.

The straight chain secondary alcohol derivatives are compared in physical properties and performance to the less degradable nonyl phenol nonionics and ethoxy sulfates and to available types of biodegradable nonionics and ethoxy sulfates.

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PERFORMANCE CHARACTERISTICS OF STRAIGHT CHAIN ALKYLBENZENE SULFONATES

W. A. Sweeney and A. C. Olson

Linear alkylate sulfonates (LAS) are discussed with regard to their detergency and foam performance in heavy-duty formulations as a function of mol wt and processing history. Physical properties are also discussed.

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METHODS FOR REMOVING DETERGENTS FROM WASTE WATERS

C. A. Brunner

A number of processes have been investigated or are being investigated for removal of alkylbenzene sulfonate (ABS) from waste waters. These can be divided into processes applicable to launderette wastes and processes applicable to municipal waste water although there is overlap.

Launderette waste treating methods include flocculation, flotation, adsorption on activated carbon or ion exchange materials, and filtration. Usually a combination of several operations is necessary for adequate ABS and suspended solids removal. Treatment costs are high, usually more than a dollar/thousand gal waste.

In municipal waste water treatment any ABS removal method must be very inexpensive. Two methods that have been used to remove most of the residual ABS after conventional sewage treatment are foaming and adding of cationic detergents. Both methods are capable of removing ABS down to levels of 0.5 ppm or less. Both have, in addition, the property of removing organic matter in addition to ABS. The cost of foaming should be less than 5¢/thousand gal for small plants and considerably less for large plants. The total cost of using cationic detergents is probably slightly higher, at least for large plants, because of the relatively high cost of these materials at the present time.

A number of other treatment methods that will remove organics, including ABS, from municipal wastes are being studied. Their costs are, in general, too high to make them applicable for ABS removal alone. However, it may be economical to reduce gross organic contaminants by these methods. Processes under study include adsorption, chemical oxidation, ion exchange, electrochemical degradation, and even distillation.

Whether specific detergent removal methods will be necessary with the advent of biodegradable detergents is open to question. With continued public demand for clean water and with the necessity of water re-use, it is certain that some of the treatment methods capable of removing organics, including detergents, from municipal waste water will be required. Where such methods are applied, any undegraded detergents and residual material left after partial degradation will be removed.

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CONDITIONS FOR HYDROGENATING CYCLIC FATTY ACIDS TO MINIMIZE AROMATIC FORMATION

R. A. Eisenhauer and R. E. Beal

Monomeric fatty acids derived from the alkali treatment of linseed oil at high temp, and containing both cyclic (1,6-disubstituted cyclohexadiene) and straight chain fatty acids, are hydrogenated to allow recovery of the liquid, saturated cyclic acids in a relatively pure state. During hydrogenation (palladium catalyst) some of the unsaturated cyclic forms aromatic fatty acids by loss of hydrogen and is not subsequently hydrogenated. The presence of substantial amounts of this aromatic in the saturated cyclic fatty acids imparts both color and oxidative instability.

A previous report described the preparation of cyclic acids free of aromatic acids by hydrogenation in the presence of a high concn of acetic acid. A further study of reaction variables was made to eliminate the acetic acid. Factors that favor the elimination of aromatic acids include a low catalyst concn, high temp and pressure, and a high ratio of substrate surface to volume. Under optimum conditions of hydrogenation the aromatic content of purified cyclic acids was ca. 1%.

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NEW METHODS FOR REFINING LINSEED OILS AND SOYBEAN OILS: VARIABLES AFFECTING THE DEGUMMING

Réné Guillaumin

Crude oils contain generally a series of fat-soluble impurities called "gums" which come from the extraction. Gums consist largely of phosphatides such as lecithin, cephalin, phosphatidic acids and sugars. A number of methods exist for removing them from oils. Generally, degumming with water or solutions of various salts is a very common practice. But in certain oils there may be a relatively high proportion of phosphatides like in soybean oils (lecithin) or in linseed oils (phosphatidic acids) and the removal of impurities from those oils is usually difficult. We describe a new process of degumming soybean and linseed oils with solutions of nitric acid and hydrochloric acid. The break free oils obtained can be used for all industrial applications in paint and varnish. An edible grade of soybean oil also can be prepared without alkali refining. About 20 oils with gums in different amounts have been tested. Observations have been made regarding the influence of the starting percentage of impurities on the degumming of crude oils.

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CONTINUOUS SOAPSTOCK ACIDULATION

J. E. Morren and D. B. Todd

A newly-developed process is described for the continuous acidulation of soapstocks derived from alkali refining of vegetable oils. Pilot plant and commercial plant results are presented for cottonseed, soybean, coconut and corn oil based soapstocks. The acidulation is accomplished by continuously reacting hot soapstock with sulfuric acid and separating and countercurrently water washing in a Podbielniak centrifugal contactor. This process offers savings in labor, sulfuric acid, and steam over conventional batch acidulation, and at the same time offers greater recovery of the available fat. Typical performance data indicate acidulated greases containing less than 0.01% mineral acid, and acid water containing ca. 0.6% mineral acid and less than 0.1% fatty acid.

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SOLVENT WINTERIZATION OF PARTIALLY HYDROGENATED SOYBEAN OILS

D. G. McConnell, C. D. Evans and J. C. Cowan

Production of a modified liquid soybean oil low in linolenic acid by solvent fractionation was investigated. Partially hydrogenated soybean oils with iodine values (I.V.) ranging from 90–105 were winterized in solvents at various temp. Pure acetone proved the best solvent for temp ranging from −16 to +6C and gave higher yields of liquid oils with optimum unsaturation and low saturated fatty acids.

Solvent fractionation allows the use of oils hydrogenated to a level that ensures almost complete removal of linolenic acid. Soybean oil hydrogenated to an I.V. of 90 and containing less than 1% linolenic acid can be winterized at +6C in acetone to yield 94% hydrogenated winterized soybean oil (HWSB) with a cloud point of −2C and an I.V. of 95.

At lower temp the yield of HWSB decreases rapidly, the polyunsaturate content increases, and the saturates decrease to low levels. Cloud points of the HWSB oils varied directly with the temp of winterization; soybean oils hydrogenated to iodine levels of 90 and 105 and winterized at −16C produced liquid oils in yields of 38 and 55% with respective I.V.'s of 106 and 118 and stearic acid contents of 1.6 and 2.3%.

Organoleptic and oxidative evaluations of the HWSB oils were compared to modified and unmodified soybean oils.

Calendar of Social Events Spring Meeting—New Orleans

Sunday, April 19, 1964

Mixer and social hour—6:30 p.m., Grand Ballroom, Roosevelt Hotel.

Monday, April 20, 1964

Past Presidents' Dinner—7:30 p.m., Royal Orleans Hotel. Free evening for other members.

Tuesday, April 21, 1964

Luncheon followed by golf tournament—12:00 noon, Timberlane Country Club (West Bank).

NASA Michoud tour. Leave hotel 1:30 p.m., return by 5:00 p.m.

Hospitality Room—1:00 p.m. to 5:00 p.m., Red Oak Room (coffee and soft drinks available).

Banquet, floor show, followed by dancing—7:30–12:00 midnight, International Room, Roosevelt Hotel.

Wednesday, April 22, 1964

Awards Luncheon—12:30 p.m., Grand Ballroom, Roosevelt Hotel.

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EQUIPMENT CHANGES REQUIRED IN CONVERTING EXISTING HEXANE EXTRACTION PLANTS TO THE HEXANE-ACETONE-WATER EXTRACTION PROCESS

E. A. Gastrock, E. L. D'Aquin, E. J. Keating, D. E. Cross and H. L. E. Vix

New processing concepts will be required in converting existing hexane extraction plants to the hexane-acetone-water extraction process based on recent pilot plant studies. These are governed largely by the desired quality criteria of the new products and by the physical characteristics of the new solvent mixture. Anticipated processing and equipment changes include: use of substantially hull-free meats; mild tempering of meats and pneumatic "crisping" of flakes; use of a second, total immerision type of extractor following the basket extractor, provided ultra low residual lipids are required; and use of a specially devised but simple method and equipment for solvent analysis, control and remake. Existing conditioning equipment, flaking rolls, basket extraction equipment, oil and meal desolventizing equipment and miscella refining equipment in existing plants can be used in the new process.

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CONVERSION TO HEXANE-ACETONE-WATER EXTRACTION OF COTTONSEED: PRELIMINARY COST STUDY

K. M. Decossas, L. J. Molaison, E. A. Gastrock and H. L. E. Vix

Equipment and total plant specifications and costs are given for conversion to hexane-acetone-water extraction of cottonseed. Conversion of hypothetical solvent extraction plants of various basket types having capacities for processing flakes from 200 and 400 tons of cottonseed/day is considered for the production of meals at two levels of residual lipides.

A process flowsheet and material balance on which the cost estimates are based are presented and discussed. Estimates of increase in operating cost are given and compared with expected increase in product value. Profitability and payout time are charted for various annual productions.

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THE EXPANSION AND EXTRACTION OF RICE BRAN

M. A. Williams and S. Baer

Rice Bran is a readily available oil-bearing material containing a good quality oil which can find many uses. It is, however, difficult to process due to a number of problems associated with the bran, particularly with the solvent extraction of rice bran. These problems emanate from two basic characteristics of rice bran: 1) the presence in the bran of a lipolytic enzyme which cause a rapid rise in free fatty acid levels, and 2) the finely granulated nature of the bran. Recent work with rice bran has indicated that cooking would correct these problems by deactivating the enzyme and agglomerating the fines.

The work discussed evaluates expansion, as obtained in an Anderson Expander, as a method of pretreating rice bran for extraction. It was found that the expanded bran showed no rise in free fatty acid level even when stored at room temp, in open containers, for a period of months. Spot tests conducted at one year and one and one-half years of storage indicated only a slight increase in free fatty acid. It was also found that expansion agglomerated the bran into particles large enough to eliminate fines and yet allow good extraction rates and good percolation rates during extraction.

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CRAMBE SEED PROCESSING: FILTRATION-EXTRACTION ON A BENCH SCALE

L. D. Kirk and G. C. Mustakas

Crambe abyssinica is a potential source of erucic fatty acid and of good quality protein provided satisfactory methods for processing the seed can be developed. Among the methods currently under study is that of filtration-extraction, a direct solvent process for high-oil content seeds.

Good oil recovery was accomplished by a series of processing steps including dehulling, flaking, cooking, drying, crisping, and extracting with hexane. When the cooking procedure was modified to include a pre-enzymatic hydrolysis step for the decomposition of naturally occurring thioglucosides, oil recovery was more difficult. Low residual oil content in the meal, however, was achieved after suitable process modification. Filtration rates of up to 2,000 lb/hr/sq ft were obtained, which should be acceptable for a commercial process.

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STUDIES ON THE RATES OF GOSSYPOL AND OIL EXTRACTION FROM RAW COTTONSEED FLAKES BY THE ACETONE-HEXANE-WATER AZEOTROPE

V. L. Frampton, A. B. Pepperman and W. H. King

Data are reported to show that the extraction of cottonseed oil from raw cottonseed flakes with the acetone-hexane-water azeotrope in a 3 or 4 step countercurrent operation is quantitative. Meals with 0.1% or less residual oil are produced in extraction operations that occupy a total of about 2½–3 min time. Total gossypol is also reduced to low levels under the extraction methods employed. Meals containing from 0.09–0.30% were obtained from seed that contained over 1% total gossypol. Available lysine levels of the meals range from 4.3–4.4 g/16 g meal nitrogen. Oils obtained through the use of the azeotrope are readily refined and bleached, and neutral oil yields are superior to those obtained with petroleum naphthas.

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Spring Meeting Offers Visit to Space Agency

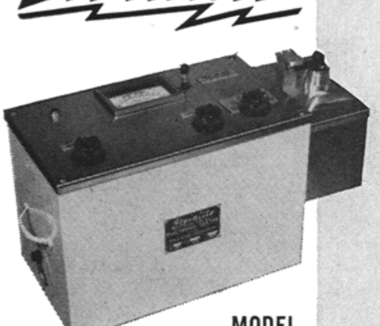
An exceptional opportunity will be available to members attending the New Orleans Spring Meeting to visit a key installation in the nation's space program. Arrangements have been completed by the New Orleans Committee for a tour of the Michoud Plant, operated by the Boeing Co. and Chrysler Corp., Space Division, for the National Aeronautics and Space Administration. In this plant, in New Orleans East, 20 miles from the downtown area, the giant Saturn booster rockets, for use in the Gemini two-man space programs, are constructed.

The tour will be conducted by NASA personnel and will be limited to 48 persons owing to restrictions on the number of visitors that can be handled by the Agency. Tickets accordingly will be made available at the registration desk, on a first come-first served basis, to registrants for the Meeting. A charge of $1.00 each will be made for the available tickets, to cover the cost of bus transportation to and from Michoud.

The tour will depart from the Roosevelt Hotel at 1:30 p.m. on Tuesday, April 21 in a specially chartered bus, and will return to the hotel by 5:00 p.m. Those taking the trip will be given a guided tour through the Michoud plant, during which they will see two Saturn boosters being constructed. NASA personnel will explain and describe the operations underway and other facilities that will be shown.

Members who wish to take advantage of the opportunity to view the Michoud operations are advised to obtain their tickets promptly upon arrival at the Registration Desk in the Roosevelt Hotel. We must observe the limitation to 48 participants, as required by NASA.

An alternate harbor trip aboard the yacht, Good Neighbor, is planned for departure at 2:00 p.m., Tuesday, April 21. $1 for transportation to waterfront and trip.



Program Abstracts . . .

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MODERN TECHNIQUES FOR THE PRODUCTION OF CRUDE TALL OIL

R. E. Thrush

A short background of the methods for the production of crude tall oil is given. A simplified flow sheet of the continuous acidulation process is shown and a new type centrifuge is introduced for the continuous separation of the various components of the acidulated sulphate reaction mixture. The separation section of the process is described with particular emphasis given to the operation of the centrifuge.

Performance of the process is discussed with respect to yield and quality of the crude tall oil.

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TALL OIL IN COATINGS' VEHICLES

G. H. Eick

Drying studies comparing long, medium, and short oil range of isophthalic acid versus phthalic anhydride, and tall oil fatty acid vs. soya oil and/or soya fatty acids, are presented. Particular emphasis is placed upon some of the premium grade tall oil fatty acids which now show signs of drying equal to or slightly better than the soya oil, in a long oil alkyd, after the driers are allowed to "condition" for a period of 48 hr.

A comparison of tall oil rosin vs. wood and gum rosin, in a number of modifications, are exemplified. Proper mixing technology in processing tall oil derivatives are stressed.

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THE ROLE AND APPLICATION OBJECTIVES OF COMPUTER CONTROL IN THE PROCESS INDUSTRIES

Musa Marto

Experience in computer control in the process industries has shown a wide variety of application objectives. The role and functions of computer control from the standpoint of data acquisition, unit control and plant wide control is discussed. Typical application areas and techniques developed will be reviewed.

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AUTOMATED BATCH TYPE ACIDULATION PLANTS

J. P. Krumbein

Automated batch type skimmings acidulation plants provide an economical and flexible tall oil process offering comparatively low capital investment, low operating costs, simplicity of operation, and high tall oil yields. These plants are particularly well suited for mills having a tall oil capability in the range of ca. 1200 tons/month or less. Above this figure, the use of the continuous process employing a continuous reactor and centrifugal separation of the oil-salt water phases may be more attractive. Automation is achieved by the use of a timer operated positive skimmings charge pump, time operated sulfuric acid charge pump, automated water metering, automated reactor temp control, electrically interlocked pumps, and continuous gravity separation of the oil-salt water phases. A shaker screen is employed to separate lignin and fibers from the tall oil prior to the phase separation step.

Three automated batch plants of the type described are now in operation.

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TALL OIL ACIDS IN SOME NEW COATING SYSTEMS

W. M. Kraft, Alex Forschirm, and Edward Janusz and Daniel Sughrue

Tall oil fatty acids have been used in this study in the formulation of a number of new coatings resins. In epoxy esters derived from a terpene-phenol glycidyl ether several compositions for use in resistant air dried and baked finishes are described.

In the urethane alkyd type, fast drying vehicles with unusual hardness and flexibility have been prepared by a new procedure. The contribution of tall oil acids to resistant alkyd finishes is described. Specific utility in the metal primer field is highlighted for these materials.

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SEPARATION OF MIXTURES OF HIGH-BOILING MATERIALS IN HORIZONTAL FRACTIONATOR

E. W. Eckey and R. J. Woestman

The fractionation of tall oil, like that of other high-boiling mixtures that must be distilled under vacuum, ordinarily requires a long column, relative to the number of plates theoretically required. A fractionator is described having the features of close spacing of individual stages, vigorous mixing at each stage, short time of exposure of liquid to high temp, and low pressure drop.

Some pilot-plant data for vacuum fractionation of binary mixtures of pure materials, and of tall oil, are presented. These indicate that applying this type of fractionator to the practical refining of tall oil may be expected to reduce the operating expenses and improve the yield of rosin and fatty acid. The low pressure drop allows the fractionation to be done with a reduced quantity of sparging steam, or without any.

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MECHANICALLY AIDED THIN FILM EVAPORATION AND ITS APPLICATION TO THE TALL OIL INDUSTRY

L. E. Najder

Heat sensitive or viscous material are fertile fields for thin film evaporators. Typical examples: tall oil, fatty acids, amines, esters, rocket fuels and radioactive wastes. Processes include dehydrating, deodorizing, decoloring, stripping and concentrating. There has been some misconception regarding thin film evaporation. It is not exotic. This has been proven. Cost is higher than conventional evaporators, but special conditions justify selection. Sometimes it is mandatory.

Compiling criteria for using these units is difficult. Extremely high heat transfer rates are characteristic, but viscosity has an effect. Evaporative rates to 100 lb/hr/sq ft have been obtained but drop to 10–20 lb/hr/sq ft for viscous products. It is ideal for heat sensitive materials since contact time is very short.

Molecular distillation is highly specialized. These units vary in construction but each is designed to produce a thin film. One uses high speed fanning action while another uses floating wiper blades. Size is a limiting factor and feed rates vary with evaporation rates.

A system consists of feed tank, gear type feed pump, rotometer, preheater or degasser, evaporator, condenser and gear pump and receiving tank for residue. The vacuum system may be a multiple stage steam jet or a compound vacuum pump. There are no definite guide posts for application in the tall oil industry. The field is large and there are many problem products.

It is being used in removing pitch from waste tall oil. Economics vary and market conditions must be analyzed. Our unit is also used in separating dimers and trimers from monomer in tall oil fatty acid. Specialty products from tall oil fatty acids are a good application. Removing color bodies is one; removing impurities from certain fatty acids is another. Finally distillation of rosin to improve color and color stability at a satisfactory yield.

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DIMER ACID STRUCTURES. THE DEHYDRO-DIMER FROM METHYL STEARATE AND DI-t-BUTYL PEROXIDE

S. A. Harrison, L. E. Peterson and D. H. Wheeler

Previous work by Sutton, and by Harrison, McCaleb and Wheeler has shown that methyl stearate is converted to dimers plus higher polymers by the action of di-t-butyl peroxide. The latter suggested that in the dimer, there was considerable linkage at carbon 2, the carbon α- to the $COOCH_3$ group, since the dimer ester was incompletely saponified by the usual procedures.

Further proof of α-linkage is presented in the present study. A fraction which is predominantly α,α'-linked dimer was isolated as the nonpolymeric cyclic anhydride (α,α'-dicetyl succinic anhydride) by molecular distillation from the linear polymeric non-α-linked polyanhydride. The isolated cyclic anhydride appeared identical with a synthetic α,α'-dicetyl succinic anhydride, whose synthesis is described.

The original dimer ester, the α,α'-cyclic anhydride fraction, and the dimethyl ester derived from it, were examined by mass spectrometry. The expected mol wt were confirmed by the parent ion peaks. Fragmentation patterns indicated appreciable α-linkage in the original dimer ester, and almost exclusive α-linkage in the ester from the isolated cyclic anhydride. Aside from preference for the α-position, joining appears to be randomly distributed.

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DIMER ACID STRUCTURES. THE THERMAL DIMER OF METHYL 10-t, 12-t LINOLEATE

R. F. Paschke, L. E. Peterson and D. H. Wheeler

Thermal dimerization of the conjugated 10-t, 12-t linoleate (250C, 5 hr) produced a dimer whose structure is shown to be that of the Diels-Alder reaction between two molecules of monomer, with one molecule acting as diene, and either one of the two double bonds of the second molecule acting as dieneophile. This produces four skeletal isomers of a tetrasubstituted (1,2,3,4) cyclohexene structure with α-β unsaturation on one chain. The isomers formed depend on whether the 10- or the 12-double bond acts as dieneophile, and whether the monomers add "head to head" or "head to tail." Evidence for the structures include chemical analyses, IR and UV spectrometry and particularly mass spectrometry of the distilled dimer, of the completely hydrogenated dimer, and of the aromatized dimer formed by catalytic dehydrogenation. The hydrogenated dimer can be separated into two components by TLC. These are probably related to "head-to-head" vs. "head-to-tail" addition.

Calendar of Ladies' Program Spring Meeting—New Orleans

Monday, April 20, 1964

Assembly and Continental Breakfast, 9:00–10:00 a.m., Blue Room, Roosevelt Hotel.

18th Century New Orleans—Guided walking tour of French Quarter.

Luncheon—Brennan's Restaurant on Royal Street.

Tuesday, April 21, 1964

Assembly and Continental Breakfast, 9:00–10:00 a.m., Blue Room, Roosevelt Hotel.

20th Century New Orleans. Bus tour of Lakefront area, parks, and fountains.

Luncheon—Vista Shores Club on Bayou St. John. A surprise in entertainment.

Wednesday, April 22, 1964

Assembly and Continental Breakfast, 9:00–10:00 a.m., Blue Room, Roosevelt Hotel.

19th Century New Orleans. Private street car tour—St. Charles Avenue, Garden District, Universities, Audubon Park, and Carrollton District.

Coffee Party—Cornstalk Room, Delmonico's Restaurant on St. Charles Avenue.

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OBSERVATIONS ON THE DICARBONYL COMPOUNDS FORMED IN AUTOXIDIZED METHYL LINOLEATE

W. Y. Cobb and E. A. Day

Methyl linoleate was oxidized at 45C in a Warburg apparatus to the point of max oxygen uptake. The oxidized ester was then vacuum steam distilled (45C, 20 μ Hg), and the distillate refluxed with an excess of 2,4-dinitrophenylhydrazine reagent. Chloroform-extractable hydrazones from the reaction mixture were thereafter passed over a cation exchanger, followed by magnesia column chromatography. The pot residue from the distillation was passed over alumina 2,4-dinitrophenylhydrazine reaction columns. The dicarbonyl monohydrazone fraction thus collected was refluxed with excess hydrazine reagent, and finally extracted with chloroform.

Dicarbonyl osazone mixtures were fractionated on Celite-ethanol-amine columns with variation of the column water content to facilitate derivative movement. Individual fractions were characterized by combinations of the following techniques: UV maxima in $CHCl_3$, ultraviolet maxima in ethanolic base, TLC, partition column co-chromatography with authentic compounds, IR spectroscopy, and mp.

Tentatively identified compounds include glyoxal, methyl glyoxal, C_5-C_9 α-keto alkanals, and *cis* but-2-ene-1,4-dial. Semiquantitative data will be presented for most of the steam distillate and pot residue dicarbonyls.

Possible mechanisms of formation of dicarbonyls will be discussed in the light of recent results.

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ALKALINE ISOMERIZATION OF METHYL CREPENYNATE (METHYL cis-9-OCTADECEN-12-YNOATE)

K. L. Mikolajczak, M. O. Bagby and I. A. Wolff

Alkaline isomerization of methyl crepenynate (methyl *cis*-9-octadecen-12-ynoate) has been studied under various conditions of temp, time, and concn of alkali and of sample. Conversion of this acetylenic acid to a conjugated triene is faster and more complete than alkaline isomerization of linolenic acid. The methyl ester of the isomerization product readily absorbs three moles of hydrogen to yield methyl stearate. The ester product has an unexpected composition as evidenced by its unusual IR spectrum. Furthermore, the rearrangement produces a preponderance of one highly labile, positional isomer.

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CIS-TRANS ISOMERIZATION OF OLEIC ACID BY NITROUS ACID

Carter Litchfield, R. D. Harlow, A. F. Isbell and Raymond Reiser

The HNO_2-catalyzed *cis-trans* isomerization of oleic acid was studied to determine its possible utilization for the commercial production of a fatty acid of high *trans* content. For the work, HNO_2 was generated *in situ* by reacting $NaNO_2$ with a strong acid. The influence of time, temp, agitation, amt of $NaNO_2$, and type of strong acid on the reaction were investigated. Maximum *cis-trans* isomerization with min by-product formation was obtained when 100 g oleic acid was reacted with 4.8 ml 2M $NaNO_2$ and 3.2 ml 6M HNO_3 for 30 min at 65C with vigorous agitation. After isomerization, nitrogenous reaction by-products were removed by passing a petroleum ether solution of the reaction products through a bed of silicic acid.

Using these optimum reaction and purification procedures, 100 g technical oleic acid yielded 93 g of product containing 60% *trans* monoene. (Since technical oleic acid contains only 82% monoene, this *trans* content represented equilibrium isomerization.) Subsequent solvent recrystallization produced 24 g 97% *trans* material.

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POTENTIAL SYNTHETIC LUBRICANTS: ESTERS OF C_{18}-SATURATED CYCLIC ACIDS

J. P. Friedrich, E. W. Bell and L. E. Gast

A series of esters were prepared from C_{18}-saturated cyclic acids (I.V. <1) containing <1% saturated straight chain acids and no aromatic contaminants. Straight chain primary and branch chain alcohols C_4–C_7 and 2,2,2-trifluoro ethanol were used to make the esters, as well as C_{18} cyclic alcohols prepared from cyclic acids. Redistilled samples of the best alcohols commercially available were used, and the esterification was carried out with a BE_3-etherate catalyst. Viscosities, measured at 100 and 210F, varied from 79–143, and pour points ranged from —30 to —95F. The oxidative stability of the esters will be reported as studied at 347F with phenothiazine being used as the inhibitor. Several have qualities that recommend them as potential lubricants, especially for low-temp applications.

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CASTOR-BASED DERIVATIVES: SYNTHESIS OF SOME ACRYLATE ESTERS

Jane S. Nelson and T. H. Applewhite

Acrylate esters of various ricinoleic and 12-hydroxystearic acid derivatives have been synthesized and characterized. Alcoholysis of methyl acrylate employing acidic or basic catalysts, as described in Org Syn. *26*, 18 (1946), failed with the secondary alcohol function of methyl ricinoleate and N,N-dimethyl ricinoleamide. Thus, this alcoholysis reaction is useful in preparing monoacrylates from the primary alcohol functions of ricinoleyl and 12-hydroxystearyl alcohols, leaving the secondary hydroxyl functions intact. Acrylate formation from the secondary alcohol groups was achieved by the use of acrylyl chloride with triethylamine as a catalyst. Castor derivatives used as starting materials

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for acrylate preparation by this method include methyl esters, unsubstituted, mono- and di-substituted amides of both the saturated and unsaturated acids. The use of glacial acrylic acid was also investigated and seems to offer possible promise in acid catalyzed esterification of these alcohol functions. The preparation, isolation, characterization, and physical properties of the various castor-based acrylate derivatives will be discussed.

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RESINS FROM HYDROXYPHENYLSTEARIC ACID

F. Scholnick, H. A. Monroe, Jr., A. N. Wrigley and W. C. Ault

Hydroxyphenylstearic acid, prepared by addition of phenol to oleic acid, has been condensed with formaldehyde using acidic and alkaline catalysts. The resulting resins have mol wt corresponding to 2-3 phenolic units and are readily soluble in alcohols. Films cast from these solutions are soft and tacky even after baking at 200C.

In order to achieve greater hardness, blends were made from solutions of the phenol-formaldehyde resins and solutions of commercial epoxy resins. Crosslinking then could occur by reaction of the hydroxyl and carboxyl functions of our resins with epoxide and hydroxyl groups present in the epoxy resins. Baked films cast from these blends were hard, flexible and chemically resistant.

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THE PLASTICIZING CHARACTERISTICS OF N,N-BIS (2-ALKOXYETHYL) AMIDES OF LONG CHAIN FATTY ACIDS

R. R. Mod, F. C. Magne and E. L. Skau

A number of N-acyl derivatives of *bis*(2-alkoxyethyl) amines have been prepared, characterized, and screened as plasticizers for poly(vinyl chloride-vinyl acetate) copolymer. Included were the N,N-*bis*(2-alkoxyethyl) amides of saturated (normal and branched), unsaturated, epoxy, dimer, terpenic, and naphthenic acids as well as mixed acids from animal fats, rapeseed, *Limnanthes douglasii* seed, parsley seed, and hydrogenated cottonseed oils. All these amides, including the stearamide derivative, were compatible. Some exhibited low-temp properties comparable to the adipate plasticizers without the adverse volatility characteristics of the adipates. With the exception of the epoxystearamide derivative the N-*bis*(2-alkoxyethyl) amides were inferior to DOP in thermal stability. The N,N-*bis*(2-ethoxyethyl) stearamide is of special significance in that it seems to be the only derivative of unsubstituted stearic acid known to be applicable as a primary plasticizer.

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AN EVALUATION OF THE RIVER-DIE-AWAY TECHNIQUE FOR STUDYING DETERGENT BIODEGRADABILITY

E. A. Setzkorn, R. L. Huddleston and R. C. Allred

The ready availability of river water as a biological medium and the simplicity of the test procedure has resulted in widespread use of the river-die-away technique for studying detergent biodegradation. The accuracy and reproducibility of the test, however, has not been well defined. This information is required to establish the validity of observed differences in degradation behavior.

The present paper presents data on the accuracy and repeatability of the methylene blue analytical procedure using both the standard method and the automated version of the methylene blue method. Data are also presented showing reproducibility of the biodegradation curves obtained by replicate analysis of detergents under identical die-away conditions. The biological deviation obtained in this manner was found to exceed the analytical deviation by more than 100% in some instances.

The effect of detergent mol wt and microbial adaptation to the test substance on the degradation pattern is also discussed.

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INFRARED SPECTROSCOPIC DETERMINATION OF DETERGENT ACTIVES

C. D. Frazee and R. O. Crisler

Several IR spectroscopic methods are described for the determination and analysis of detergent actives in sewage, ground waters, and finished detergents. The methods include the determination of the ratio of straight chain to tetrapropylene chain alkylbenzene sulfonate (ABS) in detergent actives extracted from sewage, ground water and finished detergents; the determination of level and polyethoxy chain length in alkyl and alkyl phenyl ethers of polyethylene oxide condensates; and the type of alkyl group in detergent actives isolated from formulated detergents. Specific application of these methods to studies of the degradation of ABS in sewage from controlled use areas, and in studies of the rate and mechanism of degradation of the alkyl phenyl ethers and alkyl ethers are discussed.

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THE DETERMINATION OF POLYOXYETHYLENE NONIONIC SURFACTANTS IN WATER AT THE PARTS PER MILLION LEVEL

N. T. Crabb and H. E. Persinger

A method has been developed to determine the concn of polyoxyethylene nonionic surfactant (PNS) in the ppm range in a water-bacteria medium. The method has successfully determined the concn of PNS during the course of biodegradation studies using either activated sludge or river water as the bacterial source. The nonionic surfactant was removed from the water solution by countercurrent ether extraction. Detection and measurement of the PNS was accomplished using cobalt thiocyanate and measuring the absorbance of the blue cobalt-PNS complex at 620 $m\mu$ in a 5-cm absorption cell.

Optimum extraction conditions required a neutral pH and a low ionic strength. The colorimetric step required that each molecule of PNS contain at least six ethylene oxide units for color development, and since the absorbance varies with the length of the polyoxyethylene chain, the method must be standardized using the particular compound under investigation.

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SOAPS OF MONOHYDROXYSTEARIC ACID IN SYNDET COMPOSITIONS

L. I. Osipow, William Rosenblatt and F. D. Snell

Soaps of monohydroxystearic acid, prepared by sulfation of oleic acid followed by hydrolysis, offer unique advantages in syndet compositions. Unlike sodium oleate, sodium stearate, or sodium 12-hydroxystearate, the sodium soap of this monohydroxystearic acid is an effective solubilizing agent for the preparation of liquid built syndets. No decrease in detergency was observed when 50% of a conventional surfactant in a built composition was replaced by the monohydroxystearate soap. Tetrapropylene benzene sulfonate, tallow sulfate, and the oleyl ester of sodium isothionate were employed as the primary active agents in combination with lauryl isopropanolamide, polyphosphate and other builders.

Unlike sodium stearate, and sodium oleate to a lesser extent, the sodium soap of this monohydroxystearic acid does not depress the foam of built syndet compositions, unless it is used in relatively massive doses. In the absence of phosphate builders, it acts as a foam depressant.

The soaps of this monohydroxystearic acid are biodegradable. Since they can be manufactured at low cost, there appears to be merit in including them in both solid and liquid-built detergent compositions.

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CATALYTIC CONVERSION OF FATTY MATERIALS

L. I. Osipow, W. Rosenblatt and F. D. Snell

Studies are in process on the catalytic conversion (other than by hydrogenation) of fatty materials to detergent intermediates. Stearic acid, oleic acid, methyl stearate, methyl oleate, *n*-butyl stearate, and glyceryl tristearate vapors were, in separate experiments, passed through a number of different catalyst beds. These included iron oxide-alumina, chromia-alumina and molybdena-alumina at temp ranging from 400–550C. Cracking, dehydrogenation, and decarboxylation occur simultaneously. The fatty materials are upgraded to the extent that high yields of olefins and fatty acid moieties in the 10–15 carbon atom range are produced. Reaction productions were analyzed by various wet methods, including TLC, and by IR spectroscopy.

Iron oxide-alumina proved to be the most effective catalyst for the conversion to olefins. Higher yields of olefins were obtained with the esters of the fatty acids than with the free fatty acids. Analysis of liquid reaction products resulting from a single pass showed that 75–80% olefins were obtained from methyl stearate and close to 85% from methyl oleate. Fractional distillation indicated that the per cent olefins was independent of the mol wt of the fractions. With methyl stearate, 65% of the recovered product was in the range of 10–16 carbon atoms. With methyl oleate, 75% of the recovered product was in the range of 10–14 carbon atoms.

Water vapor was found to have an inactivating effect on the iron oxide-alumina catalyst, particularly with regard to dehydrogenation and decarboxylation. Thus, in the presence of steam, shorter-chain esters and fatty acids predominate.

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CONTINUOUS FEEDING, MIXING, AND SPRAY DRYING OF DETERGENT FORMULATIONS

S. J. Silvis

The production of detergent powders has become a fully continuous operation with 1) automatic and precise feeding of the various formula ingredients, 2) continuous mixing of these ingredients, and 3) continuous spray drying of the resultant slurry to yield a product of controlled density and moisture content.

A detailed description of the Ballestra process is given showing 1) automatic weigh devices for metering the individual components of the detergent formula—whether in dry powder form or liquid form, and 2) how these materials are transported to a continuous mixing unit where they are thoroughly blended and overflow to a holding tank from whence they are pumped to the spray tower. The importance of slurry temp and pumping pressure as well as the factors involved in tower design and tower operation are all related to finished product quality and process efficiency. Advantages of continuous mixing over batch mixing are stressed. Details of the automatic controls to maintain product density and rate of feed to the tower are given.

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DETERGENCY: MICELLAR RELATIONSHIPS OF AN ANIONIC-NONIONIC SURFACTANT MIXTURE

A. M. Mankowich

The micellar characteristics of the mixed micelles formed by three ratios of an anionic-nonionic surfactant mixture have been compared with the detergencies imparted by the three combinations to aqueous alkaline cleaning solutions of ca pH 12. It was found that detergency increases with increasing charge on, and number of anionic monomers in, the mixed micelle. Improved detergency appears to be connected to decreased micellar dissociation.

Size of the aggregates is obtained by an interpretation of the light scattering data based on the completeness of the interaction of the anionic and nonionic monomers to form mixed micelles and the monodispersity of these micelles.

(Continued on page 33)

Program Abstracts . . .

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GAS CHROMATOGRAPHIC ANALYSIS OF ROSIN FOR ADDUCTS AND DIMER CONTENT

R. H. Leonard, K. A. Kubitz and J. N. Rockwell

The rosin acid dimer content of rosin influences the crystallization time as determined by the Burrell-Castor gelometer. A vacuum stripping method for analysis of rosin dimer is described. Results by this method agree with the quantitative results obtained by gas chromatography.

Rosin adducts may be chromatographed on low liquid phase SE-30. Rosin dimers and rosin adducts may be chromatographed on packings prepared by silane treatment of the support. Behavior of rosin acids on these silane packings, containing no additional liquid phase, resemble very low-liquid level SE-30 packings. A packing prepared by treatment of HCl washed Chromosorb W with a 4–1 mixture of dimethyldichlorosilane and trimethylchlorosilane was useful at 375–400C and separated rosin dimers adequately to show five components.

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THE PROCESS GAS CHROMATOGRAPHY OF FATTY ACID DISTILLATION STREAMS. I. ANALYTICAL CHEMISTRY

L. D. Metcalfe and E. H. Stoll

The commercial distillation of fatty acids is usually controlled by a titer and a simple titration. Such control procedures do not always reflect the true composition of the still stream fatty acids. This is particularly true when sharp cuts are being attempted and there is a close specification on the trace acids. Gas chromatography of the fatty acid methyl esters in the control laboratory will give the required information. However, this information is often only historical and of limited value in the operation of the still.

A process gas chromatograph to monitor the stills would be the solution. The initial work on the problem led to the development of phosphoric acid-treated polyester columns. Unesterified fatty acids may be gas chromatographed with these columns. Work was then started on the design and construction of an automatic process stream analyzer for the fatty acid stills (See paper II of this series).

When this gas chromatograph was completed, it was used to monitor three still streams automatically. Chromatograms of the fatty acid streams will be shown and discussed. Quantiative results will be compared to those obtained by conventional methyl ester analysis. Some of the analytical problems encountered with the apparatus and its operation will be described.

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PROCESS GAS CHROMATOGRAPHY OF FATTY ACID DISTILLATION STREAMS II. DESIGN & CONSTRUCTION OF THE PROCESS CHROMATOGRAPH

E. H. Stoll, L. D. Metcalfe, N. E. Nuding, G. P. Hartsuch and S. H. Shapiro

When attempting to adapt the techniques of fatty acid GC analysis to a process situation, conventional instrumentation proves inadequate because of the high vaporization and melting temp of these acids. The most serious objection is the poor separation of component peaks resulting from the slow evaporation of the injected material. In an effort to resolve these problems, an instrument was designed to perform the direct analysis of distillation streams with components ranging from C_6–C_{18} in acid chain length. It features a special injector operating at 300C and the necessary sample handling facilities for process requirements at elevated temp. Using dual photocells, stream and component selection are programmed separately on a single tape of 16-mm movie film. Output from the thermal conductivity detector is integrated continuously by an electronic system which transforms peak areas to digital values through voltage to frequency conversion. Analytical information is presented as a strip chart recording and also in digital form by panel readout lamps. For convenience, a permanent record of each analysis is printed out automatically from data provided by the electronic integrator.

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NON-YELLOWING LATEX PAINTS FROM TUNG OIL. TALL OIL FATTY ACID WITH IMPROVED DRYING CHARACTERISTICS

R. O. Austin, R. S. Zetterberg and Dan Schmidt

Tall oil fatty acids contain a relatively small quantity of conjugation. Conjugation may be substantially increased by reacting tung oil and tall oil fatty acid with polyhydric alcohol. The triple conjugation of tung oil can be controlled to produce oils that have considerably improved drying properties and inherent resistance to yellowing characteristic of tall oil fatty acid.

These oils may be easily polymerized to high polymers and emulsified to produce a latex suitable for exterior water disperible paints with excellent drying properties. Addition of penetrating agents through chalky surfaces is not necessary and excellent durability can be expected.

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PLASTICIZING PROPERTIES OF ESTERS OF MONOHYDRIC ALCOHOLS AND TALL OIL FATTY ACIDS

S. T. Bauer and Randall Hastings

Tall oil fatty acid esters prepared as intermediates in our epoxy ester plasticizer program were similarly evaluated as low-temp plasticizers in polyvinyl chloride resins. Performance characteristics as primary and secondary plasticizers in polyvinyl sheeting and extruded tapes were determined on esters from methyl to heptadecyl tallate.

Results indicate that these materials impart low-temp properties which would make them of value as low-cost plasticizers in extruded and molded products where light and heat stability are not primary factors.

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SYNTHESIS AND EVALUATION OF TALL OIL FATTY ACID: FORMALDEHYDE DERIVED PLASTICIZERS

E. P. DiBella, R. Green, W. M. Kraft and R. T. Gottesman

Tall oil fatty acid was condensed with paraformaldehyde in the presence of acidic catalysts. Crude products containing free hydroxyl groups as well as polymeric material (due to the presence of interest linkages) were obtained. A product from "aromatized" tall oil fatty acid and formaldehyde was also prepared.

Plasticizer evaluations on the methyl esters of such formaldehyde condensates from oleic acid, linoleic acid, and tall oil fatty acid demonstrated that the major components of tall oil fatty acid were suitable as raw materials for plasticizer candidates. It was further shown that plasticizer performance was improved by acetylation of free hydroxyl groups. Since methyl esters proved too volatile as plasticizers in vinyl chloride sheet formulations, some ethyl, propyl and tetrahydrofurfuryl esters (in which the hydroxyl contents were lowered by acetylation) were also prepared. The esters were evaluated as plasticizers for a vinyl chloride polymer, Geon 101EP. Comparison was made to dioctyl phthalate and, where applicable to Monsanto S409 (as a typical polymeric system).

The following properties were measured: compatibility, tensile strength, 100% modulus, per cent elongation, hardness, brittle point, carbon volatility, extraction with hexane, oil and soapy water, light and heat stability. In general, the esters studied showed promise of utility as primary plasticizers for vinyl chloride polymers. They conferred a good overall balance of properties but exhibited somewhat poor heat stability and borderline compatibility.

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METAL SALTS OF TALL OIL FATTY ACIDS

S. E. Hanan and A. Fischer

The metal salts of tall oil fatty acids were introduced as paint driers during World War II. Paint industry experience reveals that oxidation-polymerization catalysts based on this readily available raw material are lower in cost, and generally equivalent in performance to naphthenates and octoates. However, the presence of rosin acids has limited the use of tall oil driers in many Federal specification applications. Manufacturing procedures, physical properties, and application of these driers in typical paint systems is reviewed.

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RECENT DEVELOPMENTS AND IMPROVEMENTS IN PRESSURE LEAF FILTERS

H. N. Haberstroh

Pressure leaf filters offer an economical solution to separation of solid and liquid phases in the processing of a wide range of chemicals including fats and oils. Recent developments and improvements, including automation, of pressure leaf filters are described.

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REPORT ON FALL MEETING OF FLAMMABLE SOLVENTS COMMITTEE OF THE NFPA

N. H. Moore

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SAFETY DEMONSTRATION

Engineer from Humble Oil & Refining Co.

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SAFETY FACTORS IN DESOLVENTIZING OF SOLVENT MEALS

Kenneth Becker

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USE OF INTRINSICALLY SAFE LOW VOLTAGE CONTROLS IN HAZARDOUS AREAS

Exhibit and Discussion by Engineering Dept., Cutler-Hammer Co.

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PRECISION AND ACCURACY—GAS LIQUID CHROMATOGRAPHIC ANALYSIS OF C_{14}-C_{18} FATTY ACID METHYL ESTERS

W. A. Pons, Jr. and V. L. Frampton

Repetitive analyses of four primary standards by GLC utilizing polyester columns and thermal conductivity detection yielded standard deviations ranging from ±0.3–0.5% corresponding to coefficients of variation of 1.0–2.0%. These data, representing an error of measurement of 1.5–3.0% at a 99% confidence level suggest a precision approaching that of conventional spectrophotometric measurements.

Proportionality factors, calculated from known mass or M concn divided by area per cent from GLC analysis, were found to be reproducible correction factors which may be generally applicable to GLC analysis of fatty acid methyl esters with polyester columns and thermal conductivity detectors.

Mass response to a thermal conductivity detector was found to decrease with either increasing mol wt for saturated C_{14}-C_{18} acids or with unsaturation among the C_{18} unsaturated acids, while M response increases with mol wt and decreases with degree of unsaturation.

The use of uncorrected area per cent data can introduce significant absolute mass errors ranging from about +11% for myristic acid to −17% for linolenic acid.

Room Assignments for Committee Meetings During Spring Meeting

Because of the fine response of the chairmen of the Administrative and Technical Committees, many of the committee sessions to be held during the Spring Meeting in New Orleans already have been scheduled. The date, time, and meeting rooms assigned for the committee sessions scheduled, as the Journal goes to press, are indicated in the tabulation below. Times indicated by "X" are times the respective rooms are not available; those indicated by blank spaces are still available for assignment for committee meetings. Chairmen who wish to schedule meetings of their committees during these periods are urged to contact General Chairman R. T. O'Connor, or Chairman W. A. Pons, Jr., Hotel Arrangements Committee, as promptly as possible.

AOCS Committee Room Assignments
Spring Meeting—New Orleans
April 19–22, 1964

Sunday, April 19, 1964	Red Oak Room	Orleans Room	Southern Pine Room	Wildcatter Room
10:00–12:00 noon	X		X	X
1:00– 2:00 p.m.	Governing Board	X	X	X
2:00– 3:00 p.m.	Governing Board	X	Tall oil sub-comm. on membership	
3:00– 4:00 p.m.	Governing Board	X	Tall oil sub-comm. on membership	
4:00– 5:00 p.m.	Governing Board	X	X	X
5:00– 6:00 p.m.	Governing Board	X	X	X

Monday, April 20, 1964	Orleans Room	Southern Pine Room	Baronne Room
8:00– 9:00 a.m.	X	X	X
9:00–10:00 a.m.			Fatty nitrogen sub-comm.
10:00–11:00 a.m.			Polymerized acid sub-comm.
11:00–12:00 noon			Epoxidized oils sub-comm.
1:00– 2:00 p.m.		Antioxidants sub-comm.	
2:00– 3:00 p.m.	Spectroscopy sub-comm.	Antioxidants sub-comm.	
3:00– 4:00 p.m.	Spectroscopy sub-comm.	Comm. fats and oils analysis	
4:00– 5:00 p.m.	Education	Comm. fats and oils analysis	
5:00– 6:00 p.m.		Bleaching sub-comm.	

Tuesday, April 21, 1964	Red Oak Room	Rex Room	Southern Pine Room	Baronne Room
8:00– 9:00 a.m.	X	X	Journal Committee	
9:00–10:00 a.m.	Standards	Industrial Oils and Derivatives	Journal Committee	
10:00–11:00 a.m.	Standards	Industrial Oils and Derivatives	Journal Advertising Comm.	
11:00–12:00 noon			Journal Advertising Comm.	
1:00– 2:00 p.m.	X	Local Section Liaison	Uniform Methods	X
2:00– 3:00 p.m.	X	Local Section Liaison	Uniform Methods	X
3:00– 4:00 p.m.	X		Uniform Methods	X
4:00– 5:00 p.m.	X		Uniform Methods	X
5:00– 6:00 p.m.	X		Uniform Methods	X

Wednesday, April 22, 1964	Red Oak Room	Rex Room	Southern Pine Room
9:00–10:00 a.m.	Instrumental Techniques		Water Soluble Protein
10:00–11:00 a.m.	Instrumental Techniques		Water Soluble Protein
11:00–12:00 noon			
1:00– 2:00 p.m.			
2:00– 3:00 p.m.	Governing Board		
3:00– 4:00 p.m.	Governing Board		
4:00– 5:00 p.m.	Governing Board		
5:00– 6:00 p.m.	Governing Board		

X—Room not available.

Symposium on Thermal Oxidation and Polymerization in Fats

Madhu Sahasrabudhe

During recent years interest has increased in studies on chemical and nutritional aspects of heated fats. When a fat is heated, as in frying, chemical alterations occur. These can be grouped under two major classes: a) degradation of glycerides into peroxides, carbonyl compounds and hydroxy acids, and b) polymerization. Extent of these changes depends upon the presence or absence of air, and duration and temp of heating. Considerable work has been carried out on the nutritional aspects of heated fats. It has also been suggested that toxicity of these fats needs further critical examination. This symposium has been planned to bring together some of the leading scientists in the field to present more recent work on the subject.

Beginning on page 4 you will find a complete listing of the papers with abstracts. Some other prominent scientists in the field who are not presenting papers have very kindly agreed to sit on a panel for discussion at the end of the symposium. Among those who have already agreed to participate are C. M. Gooding, Corn Products Co., and E. G. Perkins, University of Illinois.

In spite of the short notice of the symposium the response has been very good. Some scientists in Europe and the Far East have indicated that they would participate if the symposium is extended to a future meeting.

All indications are that the symposium will be a success.

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Food Chemical Codex Part I Now Available

Part I of *Food Chemicals Codex,* a new publication of the National Academy of Sciences, National Research Council, is now available upon a subscription basis, in loose-leaf form. Subsequent issues of the eight or ten parts will be available over the next two and one-half years at approximately four-month intervals.

Purpose of these provisional copies of this single source of standards for direct additives is to invite comments and criticisms relating to the provisional specifications before the Codex is published in a case bound book.

Part I is the initial result of a continuing effort to provide objective quality standards for chemicals added to foods to perform some desired function. Based on elements of safety and good manufacturing practice, these specifications are presented in a series of monographs supplemented by sections covering general analytical procedures and related subjects. It comprises about 100 pages, including General Provisions section, 25 monographs, and a major portion of the General Tests and related sections.

Codex is sponsored by the Food Protection Committee, and compiled by committees composed of industry, government and academic scientists. Subscription price for all parts is $25, including a double ring binder. For further information, write: J. R. Powers, Director, Food Chemicals Codex, National Academy of Sciences-National Research Council, Washington, D. C. 20418, or order directly from the Printing and Publishing office at the same address.

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GAS-LIQUID CHROMATOGRAPHY OF TRIMETHYLSILYL DERIVATIVES OF MONOGLYCERIDES AND HYDROXY FATTY ACIDS

R. D. Wood, P. K. Raju and Raymond Reiser

The use of gas chromatography for the analysis of monoglycerides and their acetylated derivatives has been limited due to their low volatility. An accurate, rapid method for the determination of a mixture of 1-mono and 2-monoglycerides so far has not been available, while the long retention time of the acetylated derivatives of long chain hydroxy fatty acids is undesirable for quantitative estimations.

A simple method for the rapid gas chromatographic analysis of isomeric monoglycerides and hydroxy fatty acids has been developed. The hydroxy compounds were converted to their respective trimethylsilyl derivatives and used directly for gas chromatographic analysis. The monoglycerides prepared from C-8,C-10,C-12,C-14,C-16 and C-18 fatty acids were resolved successfully. The isomeric 1-mono and 2-monoglycerides were also resolved. The retention time of methyl esters of hydroxy fatty acid-trimethylsilyl derivatives was one-sixth that of the untreated hydroxy esters and one-third that of the acetylated derivatives.

The advantages and applications of this new method for the rapid determination of isomeric glycerides and hydroxy fatty acids by gas chromatography in the realm of lipid research will be discussed.

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QUANTITATIVE DETERMINATION OF DOUBLE BOND POSITIONS IN UNSATURATED FATTY ACIDS

E. P. Jones and V. L. Davison

The position of unsaturation in natural fats, especially in partially hydrogenated fats, has become increasingly important to their edible and industrial utilization. The positional and geometric isomerization of bonds that occur during hydrogenation are usually estimated by cleavage of the molecules and analysis of the split products. Limitations of techniques have made it difficult to analyze all products quantitatively, and workers have usually reported only one of the cleavage products; i.e., the less volatile difunctional fragment.

By a combination of procedures, and with special attention to quantitation, we have developed a method to determine double bond positions in mono- and polyunsaturated acids. Key features include controlled oxidative cleavage, recovery of monobasic acids as salts, and their conversion to butyl esters for programmed gas-liquid chromatographic analysis. The wt of monobasic and dibasic acid found agree very closely with theory. However, at present neither malonic acid nor propionic acid may be quantitatively estimated because of the chemical instability of the former and the high water solubility and volatility of the latter.

Analyses are shown for high purity oleic, linoleic, and linolenic acids, and for conjugated and nonconjugated *cis,trans; trans,trans;* and *cis, cis* dienes. Analyses for *cis* and *trans* monoenes and for several trienes are also included.

The reproducibility and applicability of the procedure to a wide range of positional isomeric mixtures produced by partial homogeneous and heterogeneous hydrogenations of polyunsaturates are discussed.

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A RAPID METHOD FOR IDENTIFYING THE FATTY ACIDS OF DEGRAS

Nicholas Pelick and J. W. Shigley

A rapid method for identifying the fatty acids of a natural fat will be discussed. Degras or wool fat was chosen for analysis because of its unique distribution of neutral lipids. Thin layer chromatography, silver-ion chromatography and preparative TLC will be described in this method. The techniques of gas-liquid chromatography and the use of multiphase and programmed analysis are also used. These techniques of TLC and GLC were combined to achieve a rapid method for detecting and identifying over 90 fatty acid components in degras. Four homologous series of fatty acids were identified. They were normal straight chain acids, iso acids, anteiso acids and hydroxy fatty acids. All of the series included odd carbon member acids and unsaturated acids.

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A NEW FATTY ACID WITH UNSATURATION IN THE 3,4 POSITION

M. O. Bagby, W. O. Siegl and I. A. Wolff

Seed oil from *Calea urticaefolia* has ca. 35% isolated *trans* unsaturation. Gas-liquid chromatographic analyses indicate 31.2% of an unknown fatty acid. This new acid, isolated by countercurrent distribution, readily absorbs three moles of hydrogen to yield stearic acid. The unsaturated acid has one *trans* double bond; the other two are both *cis* and are methylene interrupted as shown by spectroscopy and lipoxidase isomerization. The usual treatment with alkali conjugates only two double bonds. Oxidative cleavage yields caproic, adipic, and malonic acids. Partial reduction of the triene with hydrazine yields a monoene mixture, from which *trans*-3-octadecenoic acid was isolated and characterized. The evidence indicates that the triene is the previously unknown *trans*-3,*cis*-9,*cis*-12-octadecatrienoic acid. Nuclear magnetic resonance spectroscopy confirmed the presence of β,γ-unsaturation.

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UREA FRACTIONATION IN THE ANALYSIS OF OILS

J. L. Iverson, Jerome Eisner and David Firestone

The methyl esters of butter, lard, olive oil, walnut oil, sesame oil, and lanolin were fractionated with urea to provide less complex fractions for examination by gas-liquid chromatography (GLC). Long chain saturated fatty acids are concn in the first fractions, while highly unsaturated fatty acids are concn in the last fractions. The procedure is simple, requires inexpensive reagents and equipment, is non-destructive, and is reproducible. Qualitative identification of components is simplified by quantitative removal of other fatty acids with similar gas chromatographic retention times. Prior fractionation with urea requires more time than routine GLC analysis, but this factor is offset by improvement of detection and estimation of trace components. Separations achieved by urea fractionation are compared with those obtained by column chromatography on silicic acid and fractional distillation reported in the literature.

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SEARCH FOR NEW INDUSTRIAL OILS. XII. FIFTY-EIGHT EUPHORBIACEAE OILS, INCLUDING ONE RICH IN VERNOLIC ACID

R. Kleiman, C. R. Smith, Jr. and S. G. Yates

Seed oil of one species in the plant family Euphorbiaceae, *Euphorbia lagascae* Sprun., contains 57% epoxy acid that has been identified as *cis*-12,13-epoxy-*cis*-9-octadecenoic acid (vernolic acid). The low percentage of trivernolin in the glycerides of *Euphorbia lagascae* oil is in sharp contrast to its occurrence as a major constituents in *Vernonia anthelmintica* oil.

Seed from 57 other species in the Euphorbiaceae have been analyzed for oil and protein contents, and the methyl esters of the derived oils have been analyzed by gas-liquid chromatography for fatty-acid composition. On the bases of these analyses, oils from 28 species contain 50–76% linolenic acid; oils from seven, 62–77% linoleic acid; and oils from three, 55–84% oleic acid. Oils from the remaining species contain lesser amounts of the common acids and no significant amounts of unusual components. Iodine values of the oils range from 87–221.

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COMPOSITION OF CORN OIL

J. B. Beadle, D. E. Just, R. E. Morgan and R. A. Reiners

The composition of commercial corn oil from USA corn is remarkably constant. A total of 103 samples of refined corn oil produced over a period of two and one-half years were analyzed by the alkali isomerization procedure. Average values were:

Iodine Value (Wijs)	Constituent Fatty Acids (% Total Fatty Acids)			
	Saturated	Oleic	Linoleic	Linolenic
123.6	13.7	29.7	55.5	0.6

Nearly 86% of the samples had an iodine value (I.V.) within a unit of the average; 93% of the linoleic acid values were within 2 units of the average. All samples contained small amounts of linolenic acid. A number of these samples were analyzed by gas-liquid chromatography (GLC). The average linolenic acid content by this method was about 2.5 units higher than that found by the isomerization method. This difference may be due to the fact that GLC responds to all C-18 dienes equally while the alkali isomerization method responds only to conjugabile dienes. Possible sources of error in both methods of fatty acid analysis are discussed.

Although much of our experience has been with the alkali isomerization method, the GLC technique is preferred because it is simpler and yields more information on fatty acid composition. A most important advantage is that determination of the I.V. of the oil serves as a check on GLC results. The I.V. calculated from the GLC results, making allowance for 1.25% unsaponifiables in the case of corn oil, should be within a few units of the Wijs value.

Oils derived commercially from corns grown in other countries are generally more saturated than those from USA corn. The I.V. of the samples examined varied from 107–125, the linoleic acid contents from 42–56%. The relationship between I.V. and linoleic acid content established by others from hydrid corns holds fairly well for these samples.

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COUNTERCURRENT DISTRIBUTION OF ALKALI-ISOMERIZED METHYL LINOLENATE WITH AN ARGENTATION SYSTEM

C. R. Scholfield, R. O. Butterfield, Helen Peters and H. J. Dutton

Linolenic acid was isomerized by heating with potassium hydroxide in ethylene glycol at 165C for 30 min. The isomerized acids were separated into urea-adduct-forming (AF) and nonurea-forming (NAF) fractions. Both were converted to methyl esters and fractionated by countercurrent distribution (CCD) between hexane and 0.2N silver nitrate in 90% methanol. Some of the CCD fractions were further fractionated by low-temp crystallization from acetone.

CCD of the AF fraction produced two main components. The first, with partition coefficient 10.7, is largely trienoate containing triene conjugation. The second, with partition coefficient 2.0, is largely trienoate containing diene conjugation. CCD of the NAF fraction produced the same two components in addition to cyclic esters with partition coefficient 5.0.

The isomerized linolenic acid is estimated to contain 36% trienoic acids with triene conjugation, 50% trienoic acids with diene conjugation, and 14% cyclic acids.

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NEW NONIONIC DETERGENTS DERIVED FROM EPOXIDIZED OILS II

K. L. Johnson

The physical and surface active properties of alkylolamides prepared from methyl 9,10-epoxystearate are discussed. These materials are prepared by reacting methyl 9,10-epoxystearate with a polyoxyethylene alcohol to produce the methyl ester of the hydroxyalkoxypolyoxyether substituted carboxylic acid which is subsequently subjected to aminolysis with diethanolamine.

The properties of the derivatives as a function of the mol wt of the polyoxyethylene alcohol are explored and appear to exhibit critical changes at a value of ca. 500. All the materials thus prepared exhibit higher water solubility than corresponding N,N-di(2-hydroxyethyl)amides and foam somewhat less.

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NEW NONIONIC DETERGENTS DERIVED FROM EPOXIDIZED OILS III

K. L. Johnson and S. E. Tierney

A series of nonionic detergents based on epoxidized sperm oil and various expoxidized lower alkyl esters of unsaturated fatty acids are presented. Materials were synthesized by alcoholysis of the oxirane oxygen in the presence of boron trifluoride. Isopropyl alcohol was used as a solvent to act as an autopolymerization inhibitor. Methoxy polyoxyethylene alcohols were used as the hydrophilic alcohols with which the epoxy compounds were reacted. In addition to the characterization of the reaction and its products, the physical properties and performance characteristics of the various compounds synthesized are presented. Although no data are available at this time it is felt that these materials are definite candidates for biodegradable nonionic detergents.

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THE PREPARATION AND ANALYSIS OF ALKANOLAMIDES

H. D. Russell, H. G. Scholten, R. A. Mount and M. N. Cruse

Fatty diethanolamides are nonionic surface active agents which are widely utilized as foam stabilizers, emulsifiers, viscosity builders, etc., in such products as laundry detergents, dishwashing formulations, shampoos and cosmetics. In order to better understand the commercial reactions used to produce fatty diethanolamides, chemists at the Technical Service and Development Laboratory, Dow Chemical Co., undertook a study of the amide formation reactions: 1) between lauric acid and diethanolamine to produce the "Kritchevsky-type" condensate; and 2) between methyl laurate and diethanolamine, catalyzed with sodium methylate, to produce the high purity or "super" amides. The effects

(Continued on page 44)

Spotlighting the Tall Oil Symposium

J. P. Krumbein

The 1964 Tall Oil Symposium is the second such presentation sponsored by the AOCS, the first having been presented at the 1958 Annual Meeting. The excellent reception of the first symposium, combined with the fact that the tall oil industry has continued its growth rate in the intervening six years, indicates that the time is opportune for a second presentation.

Illustrating the tall oil industry growth rate is the fact that tall oil output in 1957 was 337,000 tons, whereas in 1963 the output was 450,000 tons. Estimated tall oil fatty acid output has increased from 76,000 tons in 1959 to 120,000 tons in 1963. The importance of tall oil fatty acids is therefore most evident.

The symposium program can roughly be divided into several categories, as follows:

1) Production of crude tall oil from skimmings.
2) Use of computers in process operations.
3) Novel equipment which can be used in the distillation of tall oil.
4) Latest advances in gas chromatography, particularly as it pertains to the continuous analysis or monitoring of fatty acid process streams from the distillation operations.
5) End use of tall oil products and derivatives.

Titles and abstracts of the 15 papers included in the Symposium (two sessions) can be found in the Program, beginning on page 4. Papers to be presented have been screened for general interest, and it is believed the Symposium will be of considerable interest to much of the membership.

Program Abstracts . . .

(Continued from page 38)

of temp, pressure, mole ratio of reactants, catalyst concn, and inert gas sparging upon the rate of reaction were studied. Analytical procedures were developed using IR and near-IR spectroscopy and gas chromatography as well as some wet chemical methods of analysis to follow the course of the reactions. Results of these studies and the analytical procedures will be discussed.

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DISODIUM 2-SULFOHEXADECYL AND 2-SULFOOCTADECYL SULFATES

A. J. Stirton, F. D. Smith and J. K. Weil

1-Hydroxy-2-alkanesulfonic acids from the metal borohydride reduction of esters of α-sulfopalmitic and α-sulfostearic acid were sulfated with chlorosulfonic acid to give disodium 2-sulfoalkyl sulfates $RCH(SO_3Na)CH_2OSO_3Na$. The solubility, surface and interfacial tension, critical micelle concn, calcium stability, metallic ion stability, stability to hydrolysis, wetting, foaming, detergent and lime soap dispersing properties were measured.

The 16 and 18 carbon disodium 2-sulfoalkyl sulfates were found to be similar to the isothionate esters of α-sulfopalmitic and α-sulfostearic acid $RCH(SO_3Na)CO_2CH_2CH_2SO_3Na$ in general structure and surface active properties. The general structure, a long hydrophobic chain which terminates in two bulky adjacent hydrophilic groups, is evidently related to the excellent lime soap dispersing agent properties which both disodium 2-sulfoöctadecyl sulfate and disodium 2-sulfoethyl α-sulfostearate have in common.

Compared to sodium octadecyl sulfate, the presence of the sulfo group in disodium 2-sulfoöctadecyl sulfate greatly increases solubility and critical micelle concn, and thereby affects all surface active properties with some loss in detergency but with greatly improved metallic ion stability and lime soap dispersing properties. Like the sodium alkyl sulfates, the disodium 2-sulfoalkyl sulfates are stable to alkaline hydrolysis but can be hydrolyzed at about the same rate in acid solution; disodium 2-sulfoethyl α-sulfostearate was stable to acid hydrolysis under the same conditions.

Disodium 2-sulfoöctadecyl sulfate and disodium 2-sulfoethyl α-sulfostearate are biodegradable in the River Water Die-Away test, but not as easily as sodium octadecyl sulfate since the product of enzymatic hydrolysis is surface active.

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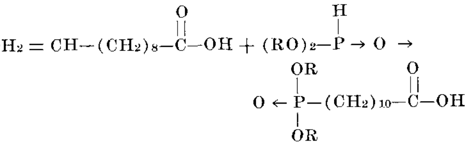
PHOSPHORUS DERIVATIVES OF FATTY ACIDS. ADDITION OF DIALKYL PHOSPHONATES TO UNSATURATED ACIDS

Richard Sasin, R. A. De Maur'ac, Eric Leopold, H. B. Gordon and G. S. Sasin

A series of dialkylphosphonoundecanoic acids was prepared by the reaction of dialkyl phosphonates with undecenoic acid under free radical conditions.



$$CH_2 = CH{-}(CH_2)_8{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}OH + (RO)_2{-}\overset{\overset{\displaystyle H}{|}}{P} \rightarrow O \rightarrow O \leftarrow \underset{\underset{\displaystyle OR}{|}}{\overset{\overset{\displaystyle OR}{|}}{P}}{-}(CH_2)_{10}{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}OH$$

R = CH_3, C_2H_5, C_4H_9, 2-Ethylhexyl

An analogous series of compounds was prepared from oleic acid and dialkyl phosphonates also under free radical conditions. Amides and substituted amides of the phosphono acids were also prepared.

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EVALUATION TEST FOR SCOURING AGENTS: FATTY SOIL ON A HARD SURFACE

J. A. Monick

A method has been developed to rate the scouring ability of abrasive cleaners on a tough fatty film which is baked onto an aluminum panel. Results are obtained on a comparative basis, and are best determined by one person using as few panels as possible for each investigation. The soiled surface was prepared by spreading 5 ml lard-chicken fat mixture on one side of the panel, and baking for 5 min at 575F. Three classes of scouring agents were studied: steel wool with soap, silex which was resin-bonded to nylon fiber, and silex on a dish cloth. Results can be expressed as scouring efficiency, and related to an arbitrary standard designated as 100%.

— 90 —

AN AMPEROMETRIC TITRATION METHOD FOR BLEACH EVALUATION

D. J. Sargent

An analytical method has been devised as rapid screening procedure which predicts how effective an active chlorine-containing compound will be as a bleaching agent. The method is based on an amperometric titration which indicates bleaching performance from both the increase in whiteness and fabric tendering standpoints. Excellent correlation was obtained between amperometrically determined data and practical bleaching data for several extensively used bleaching agents. In connection with this amperometric titration method, a polarographic method is also presented which provides good correlation between the polarographically determined data and practical bleaching data.

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CONSUMER EVALUATION OF LIQUID SYNDETS II

K. L. Johnson and H. P. Andrews

Six proposed candidates for nonionic biodegradable surfactants have been evaluated using a consumer panel. The formulations studied explore the performance of these materials in the presence of a fatty-based alkylolamide foam stabilizer and biologically "soft" alkyl aryl sulfonate at two levels of nonionic concn. The samples were distributed in pairs accompanied by a facial expression data sheet requesting evaluation of the foaming, general performance and dermatological properties of each. Every sample was compared with every other sample twice in a duplicated balanced incomplete block design evaluating each of the twelve combinations for the 2 x 6 factorial experiment. The nonionic detergents evaluated are all polyoxyalkylated alcohols, including products of natural and synthetic origin. Products based on unsaturated and secondary alcohols are included. Laboratory data were also obtained covering foaming, wetting and surface tension. A full statistical interpretation of the main and interactive effects is presented.

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DETERIORATION OF CORN OIL UNDER ASSIMILATED RESTAURANT DEEP FAT FRYING CONDITIONS

R. G. Krishnamurthy and S. S. Chang

One of the major difficulties in the study of the effect of heated oil upon the metabolic pattern of lipids is to obtain oil samples produced under laboratory conditions which are comparable to commercial operations of deep fat frying of foods. After a number of preliminary experiments, a laboratory apparatus has been built which can be used to study the chemical reactions involved in the deep fat frying under assimilated restaurant operations. The volatile decomposition products evolved can be collected by this apparatus for chemical characterizations.

In order to first study the chemical reactions of the frying oil without its interaction with the food fried, cotton balls containing 75% by weight of water were fried every 30 min in corn oil maintained at 185C. Fresh corn oil was used to replenish the oil absorbed by the cotton balls every 12 hr.

The chemical characterization of the volatile decomposition products thus collected and the physical and chemical changes of the frying oil under these conditions will be presented.

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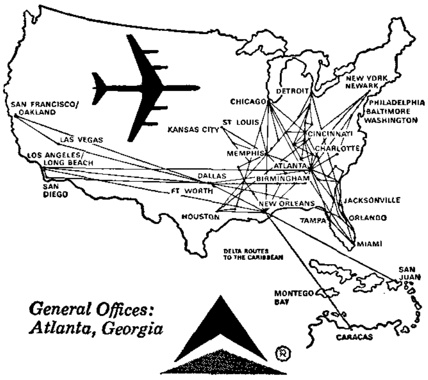
CARBONYL COMPOUNDS FORMED DURING DEEP FRYING

L. A. Wishner and Mark Keeney

Fresh commercial corn oil, fresh commercial lard, and hydrogenated vegetable shortening were analyzed for carbonyl compounds before and after the deep frying of 3400 g potatoes at 200C in 300–400 g batches.

(Continued on page 48)



Program Abstracts . . .

(Continued from page 45)

Frying was carried out in an apparatus with a capacity for 2000 g fat and designed to quantitatively trap volatile materials which would ordinarily escape during frying. The trapped distillate was also subjected to carbonyl analysis.

Analysis of the fats and distillates showed a carbonyl pattern in essential agreement with the classical autoxidation mechanism for the different fats, i.e., the typical alkanals, alk-2-enals, and alk-2,4,-dienals. The dominance of this process over that of thermal oxidation was also indicated in the carbonyl pattern by the absence of alk-1-ene-3-ones and other thermal oxidation products. The comparison of the concn of the carbonyl compounds in the fats before and after frying and in their distillates indicates that the deodorization process which accompanies deep frying may be efficient in preventing the accumulation of toxic concn of the oxidation products in fats which have been in continued use.

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A LONG-TERM NUTRITIONAL STUDY WITH FRESH AND MILDLY OXIDIZED VEGETABLE AND ANIMAL FATS

H. Kaunitz, R. E. Johnson and L. Pegus

Matching groups of male albino rats were fed purified diets containing fresh or oxidized cottonseed oil, olive oil, chicken fat, or beef fat for two years. The oxidized fats were prepared by aeration at 60C for 40 hr. This mild oxidation was selected in order to approximate what might occur to the fats under unfavorable conditions of storage and use. The rats were observed for wt gain, food intake, and survival rate. Periodically, six rats were sacrificed from each group and examined for organ wt and pathology. Their sera and tissues were examined for cholesterol, total lipid, and fatty acid composition of the latter; the depot fat triglycerides of those rats sacrificed after 70 weeks on the diet were examined for their molecular structure, as were those of the dietary fats. Mineral analyses were also carried out on serum and tissues.

Several of these parameters were affected by the kind of fat fed and/or its state of oxidation.

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NUTRITIVE VALUE OF HEAT POLYMERIZED VEGETABLE OILS

N. V. Raju, M. Narayana Rao and R. Rajagopalan

Peanut, sesame and coconut oils were heated at 270C for 8 hr in an open iron pan. These fats were fed to albino rats at 15% level in otherwise adequate diets. All rats fed heated fats showed a growth depression. Livers of rats receiving the heated oil were congested and showed extensive periportal fatty infiltration. Rats on heated peanut oil showed 1) reduced B-vitamin storage in the liver, 2) increased glucose and cholesterol levels in the blood, and 3) a disruption of digestion and absorption of carbohydrate.

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CHROMATOGRAPHIC STUDIES ON OXIDATIVE AND THERMAL FATTY ACID DIMERS

C. D. Evans, D. G. McConnell, E. N. Frankel and J. C. Cowan

A chromatographic study was carried out to investigate the nature and possible estimation of nonvolatile polymeric products in edible oils. This information may be helpful in any evaluation of changes that result from oxidation and thermal treatment of oils during processing and storage.

Dimers obtained by low-temp oxidation of methyl linoleate were compared in their chromatographic behavior to thermal dimers prepared by high-temp polymerization of conjugated methyl linoleate. Distilled dimers of each were subjected to liquid-partition chromatographic separations on silicic acid columns as methyl esters, as free acids, and as methyl esters prepared by saponification and re-esterification. Chromatographically isolated dimers were also rechromatographed before and after each treatment.

When thermal dimer esters are saponified and re-esterified, chromagraphic recoveries are quantitative, and the expected changes in polarity result; whereas, with oxidative dimers esters, gross changes in polarity occur. All chromatographic separations of dimer esters or their acids show four distinct areas of increasing polarity. Fractionations will be discussed on the basis of these changes in polarity for the monomers, dimers, and trimers of both the thermally and oxidatively prepared polymers.

Distilled oxidative dimers do not give highly resolved chromatographic fractions, but show a large peak (ca. 30%) of the same polarity as the thermal dimer, and have a major peak (ca. 50%) in an area of much higher polarity. Saponification and re-esterification of these two chromatographically isolated fractions show that they are not composed of homogeneous material because fractions of various polarities are recovered. When mixtures of oxidatively and thermally prepared methyl linoleate dimers are chromatographed, the experimental results agree well with those calculated from the fractionation of the component dimers. Results indicate that the nonvolatile oxidative products contain material that behaves chromatographically like a thermal dimer.

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STUDIES ON HEATED FATS

M. R. Sahasrabudhe

Interest has increased in studies on the effect of heat on edible fats. Recent reports indicate that during deep frying over extended periods, a significant portion of the oil is polymerized. Results of a study on corn oil heated at 180C and 200C will be reported. The heated oil was fractionated into 8 fractions. The first 4 fractions constituting ca. 60–80% were found to be triglycerides, the remaining 4 fractions constituted degraded and polymeric products of high mol wt.

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