

Use of Circulating Stirrers in Preparing Fatty Acids

B. S. VAN ZILE, F. W. SCHNEIDER, and E. W. BLANK

Research and Development Dept., Colgate-Palmolive-Peet Co.
Jersey City, New Jersey

In preparing the total fatty matter (fatty and rosin acids plus unsaponified matter) for rosin and titer tests, acid and iodine numbers (1), it has been our experience in this laboratory that chemists not familiar with the necessity of having the soap completely dissolved before adding the 30% sulfuric acid frequently contaminate the fatty acids with soap. The necessity for complete mixing of the fatty acids with the sulfuric acid is often only too evident when the fatty acid constants do not agree within themselves.

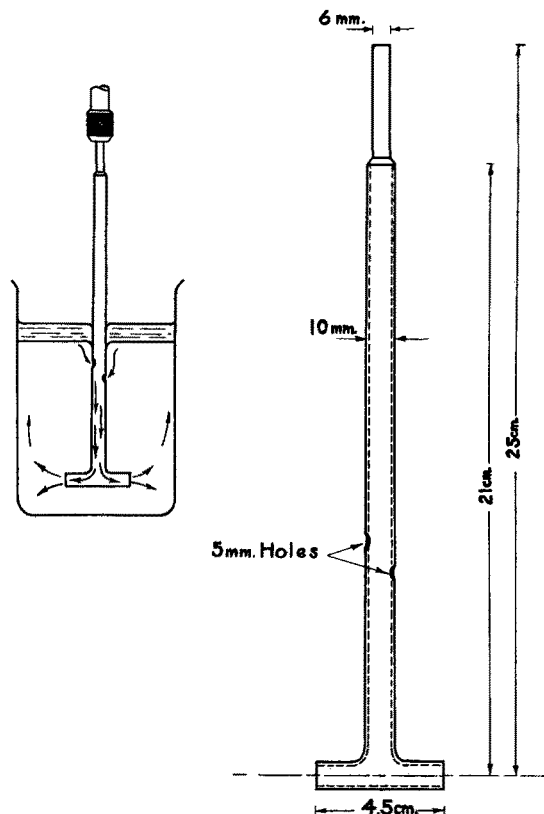
In order to avoid this error it is our practice to use a circulating stirrer in preparing fatty acids.

Figure 1 shows the constructional details and dimensions of the type of stirrer used in this laboratory. No originality is claimed for the design. Any other type of circulating stirrer will probably work as well. The small inset shows the mode of use.

The stirrer should be put into operation during the splitting operation and subsequent washing of the fatty acids. By its use complete contact of the melted fatty acids with the sulfuric acid and wash water is assured.

REFERENCE

(1) Official and Tentative Methods of the American Oil Chemists' Society, p. A-6a (1941).



Abstracts

Oils and Fats

Edited by
M. M. PISKUR and SARAH HICKS

CHEMICALS FROM FATS. A. W. Ralston. *Chem. & Eng. News* 21, 3-6 (1943).

OIL SEED ANALYSIS. II. THE MOISTURE DETERMINATION. H. P. Kaufmann and M. C. Keller. *Fette u. Seifen* 49, 93-102 (1942). A review of methods is presented. For the oven method the effect of time and temp. on the results on rape seeds is tabulated. For the distn. procedure the solvents xylol, toluol, benzol, cyclohexane, benzine (b. 90-95°) and *n*-heptane (b. 98°) were compared. Results by the titrimetric method on rape seed samples were also presented.

APPLICATION OF MICROMETHODS IN THE FAT FIELD. II. MICROMETHOD FOR THE FAT AND WATER DETERMINATION IN OIL SEEDS. G. Gorbach. *Fette u. Seifen* 49, 553-6 (1942). A review.

SOCIETY WORK OF THE DFG. 15. OIL SEEDS, OIL CAKE AND MEALS. G. Greitemann. *Fette u. Seifen* 49, 401-9 (1942). Methods for sampling, grinding and detg. fat and moisture content of domestic and imported products are given. Results of collaboration on detn.

of fat and moisture on rape seed, linseed cake and coco cake and meal are tabulated.

ANALYSIS OF OIL SEEDS. III. SIMULTANEOUS DETERMINATION OF FAT AND WATER. H. P. Kaufmann and M. C. Keller. *Fette u. Seifen* 49, 272-5 (1942). A special app. is described in which the moisture is distd. with heptane vapors and condensed in a measuring tube. Simultaneously the returning heptane is used as the solvent for the fat detn. The method is not limited to the analysis of oil seeds.

DETERMINING THE FAT CONTENT OF OIL SEEDS. A. Paleni. *Fette u. Seifen* 49, 275-8 (1942). In 12 tests the highest value for fat (39.63%) was obtained on dried seeds in a Besson extractor and with Et₂O as the solvent; the lowest value (37.11%) was obtained with a Soxhlet extractor using petr. ether. The results with the Soxhlet extractor were lower than those of the Besson app. The use of the Besson app. and petr. ether as the solvent was preferred.

DRY DEGERMINATING OF FEED CORN, A PROCESS FOR IMPROVING OUR FAT SITUATION. II. Felix Grandel. *Fette u. Seifen* 49, 5-15 (1942). The first paper (*ibid.* 47, 185-8) described a mech. means of degerminating corn so that the germ could be processed for oil while the remainder is used for livestock feeding. The present paper deals with the detn. of the germ content of corn and the degerminated product. Method: The sample of 50 kernels is fed to 1-2 month old albino rats in cages with screen bottoms of 1 cm. openings. The rats first bite of the small root ends, then eat the germ and the residue falls through the screen. The difference between the wt. of the original corn and the degerminated corn plus the root tips which can be collected below the cage is the amt. of germ. The rats proved efficient degerminers for by means of fat analyses it was demonstrated that they were more precise than is possible by hand methods. Analyses on 20 samples of various types are tabulated. Infected kernels should not be used in the test.

DETERMINATION OF THE STABILITY OF OILS AND FATS. N. D. Sylvester, L. H. Lampitt and A. N. Ainsworth. *J. Soc. Chem. Ind.* 61, 165-9 (1942). An automatic record of the O₂ absorption by oils and fats forms the basis of a method for the detn. of the induction period; the results agree with those obtained by means of peroxide detns. Data are presented on the induction period of fat mixts. and on the antioxid. effect of soya flour.

SOLIDIFICATION POINT NOMOGRAPH FOR FATTY ACIDS. D. S. Davis. *Ind. & Eng. Chem.* 35, 105 (1943).

THE MIXED UNSATURATED GLYCERIDES OF LIQUID FATS. IV. LOW-TEMPERATURE CRYSTALLIZATION OF WHALE OIL. T. P. Hilditch and L. Maddison. *J. Soc. Chem. Ind.* 61, 169-73 (1942). The component glycerides in a specimen of Antarctic whale oil have been investigated by sepg. the oil, by crystn. from acetone contg. solid CO₂ at -10°, -20°, and -30°, into 4 fractions of differing soly. and compn. and detg. the component acids present in each fraction. No approach to complete sepn. of any individual glyceride was, of course, achieved, but the chief types present were found to be as follows: "oleo"-satd.-unsatd. (C₁₄, C₁₆, C₂₀, C₂₂) glycerides, 66; "oleo"-diunsatd. (C₁₄, C₁₆, C₂₀, C₂₂) glycerides, 12; oleo-myristopalmitins, 8; satd.-di"oleins", 6; tri-unsatd. (C₁₄, C₁₆, C₂₀, C₂₂) glycerides, 4% (mol.). One unsatd. C₁₈ acid group per triglyceride mol. occurred in 86% of the triglycerides present in the oil, while 2 of these groups were present in a further 8% of the oil. About half of the oil contained no acid higher than the C₁₈ series, and about 1/3 contained 1 group per triglyceride mol. of the highly unsatd. C₂₀ or C₂₂ acids. Certain modifications are suggested in the preliminary sepn. of the acids of whale (or fish) oil prior to analysis by ester-fractionation, and in the low-temp. crystn. of fats contg. glycerides of highly unsatd. acids, in order to minimize alteration of the latter by polymerization or oxidation during the course of the exptl. work.

REFRACTIVE INDICES AND DENSITIES OF NORMAL SATURATED FATTY ACIDS IN THE LIQUID STATE. A. Dorinson, M. R. McCorkle and A. W. Ralston. *J. Am. Chem. Soc.* 64, 2739-41 (1942). The refractive indices of the normal satd. fatty acids from caproic to stearic inclusive have been detd. at a no. of temps. between

20 and 80°. For each acid the refractive indices are straight line functions of the temp. with an abrupt change of a slope at 40°. An explanation of this change of slope has been presented. The densities of these acids at 80° have also been detd. Molar vols. and molar refractivities for the homologous series have been computed and shown to be linear with respect to the no. of C atoms in the chain.

STUDIES OF HIGH MOLECULAR WEIGHT ALIPHATIC AMINES AND THEIR SALTS. IX. BEHAVIOR OF VARIOUS SALTS OF DODECYLAMINE IN WATER, ETHANOL AND BENZENE. C. W. Hoerr and A. W. Ralston. *J. Am. Chem. Soc.* 64, 2824-9 (1942). The solubilities of dodecylammonium formate, acetate, *n*-propionate, *n*-butyrate, chloride, bromide, iodide, dodecylcarbamate, primary and secondary phosphates and acid and normal sulfates, N-methyldodecylammonium chloride and N-dimethyldodecylammonium chloride and acetate in water, ethanol and benzene have been detd. The phase change of the water systems of dodecylammonium formate, acetate, propionate and N-dimethyldodecylammonium acetate have been investigated, and the hydrates formed by these salts are reported. The colloidal nature of aq. solns. of these salts has been demonstrated by a study of their osmotic coeffs. Mol. association of dodecylammonium butyrate in benzene has been discussed.

OBSERVATIONS ON THE EFFECT OF SOME SOLVENTS UPON THE ACYLATION OF PHENOL WITH HIGH MOLECULAR WEIGHT ACID CHLORIDES. A. W. Ralston, A. Ingle and M. R. McCorkle. *J. Org. Chem.* 7, 457-61 (1942). Friedel-Crafts acylations of phenol have been conducted with even- numb. acyl halides from caprylyl to stearoyl chlorides inclusive in tetrachloroethane, nitrobenzene and CS₂ in the presence of excess Al₂Cl₆ and the results compared. Nitrobenzene exerts a much greater *p*-directing influence than CS₂. Acylations of phenol with acyl chlorides of higher mol. wt. than caprylyl chloride in tetrachloroethane gave only resinous products. The length of the alkyl chain does not exert an influence upon the ratio of *p* to *o*-isomers obtained when phenol is acylated under the conditions described.

REARRANGEMENT OF PHENYL CAPRYLATE WITH FERRIC CHLORIDE, TITANIUM TETRACHLORIDE, STANNIC CHLORIDE AND ZINC CHLORIDE. A. W. Ralston, E. W. Segebrecht and M. R. McCorkle. *J. Org. Chem.* 7, 522-7 (1942). The activity of FeCl₃ is comparable to that of Al₂Cl₆ for this rearrangement; Ti tetrachloride is appreciably less active and both stannic and Zn chlorides are only weakly catalytic. FeCl₃ produces a much higher ratio of *p*-hydroxy ketones to *o*-hydroxy ketones than Al₂Cl₆ or Ti tetrachloride. Caprylic acid and *p*-caprylylphenyl caprylate are among the products formed during the rearrangement of phenyl caprylate with either Ti tetrachloride or SnCl₄.

FATE OF MANNIDE MONOOLEATE IN THE ANIMAL BODY. W. E. Evans, H. Wollenweber, M. Ruppertsberger and J. C. Krantz. *Proc. Soc. Exptl. Biol. & Med.* 51, 222-3 (1942). Owing to the shortage of glycerin in England toward the close of the world war, fats were prepd. without this polyhydric alc. In the quantities administered in these expts. mannide monooleate appears to be neither acutely nor chronically toxic to the white rat and to be innocuous in the diet of the Rhesus macacus monkey. Mannide monooleate is ab-

sorbed from the intestinal tract of the white rat. No damage was observed to the important viscera of the white rat or monkey after an 8-wk. feeding period with mannide monooleate.

INFLUENCE OF ESSENTIAL FATTY ACID DEFICIENCY ON TRANSPORT OF FATTY ACIDS INTO THE LIVER. R. H. Barnes, I. I. Rusoff and G. O. Burr. *Proc. Soc. Exptl. Biol. & Med.* 51, 235-7 (1942). Rats suffering from a severe deficiency of the essential fatty acids show the same rate of incorporation of labeled fatty acids into the liver phospholipids as do rats which have been cured of this deficiency by the administration of 3 to 4 drops of corn oil for 1 month. The rate of incorporation of labeled acid into the liver phospholipids is the same for rats raised on the fat deficient diet as has been previously observed for rats receiving a regular mixed stock diet.

INACTIVATION OF BIOTIN BY RANCID FATS. P. L. Pavcek and G. M. Shull. *J. Biol. Chem.* 146, 351-55 (1942). The inactivation in vitro of biotin by a rancidified ration and by fats and Et linolate of a high peroxide no. has been studied; 96% inactivation of pure biotin could be accomplished in 12 hrs. by means of Et linolate of a high peroxide no. In the presence of α -tocopherol this inactivation amounted to only 40% after 48 hrs. incubation. The inactivated product still showed 56% activity when measured by the yeast growth method, indicating a similarity between the product formed from biotin by the action of rancid fat and by dil. H_2O_2 .

THE UTILIZATION OF FATS BY HERBIVORA. H. Paul and C. M. McCay. *Arch. Biochem.* 1, 247-53 (1942). Diets contg. as much as 30% of fat can be fed to guinea pigs. The m.p. of a fat is important in detg. its utilization by guinea pigs but not in the case of rabbits and sheep. Guinea pigs only utilize about half as much elaidic acid as oleic acid when these isomers are fed as 6% of the diet. Rats utilize the isomers equally well. In contrast to guinea pigs, rabbits and sheep digest and absorb hard fats as well as soft ones. The milk fat, secreted by cows fed cod liver oil, was well tolerated by guinea pigs. No lesions of the muscles resulted, so it is unlikely that the fraction of cod liver oil that leads to the destruction of vitamin E is secreted by a cow fed cod liver oil. Rabbits resemble guinea pigs in being able to absorb castor oil. M.p. rather than degree of satn. seems to be the detg. factor in the utilization of fats by guinea pigs. A cow fed milk-fat, secreted during a period of cod liver oil feeding, remained normal, indicating that the factor responsible for depressing the secretion of fat does not pass into the milk from the cod liver oil.

THE ANTAGONISTIC EFFECT OF LIPOCAIC AND THE ANTERIOR PITUITARY ON FAT METABOLISM. O. C. Julian, D. E. Clark, J. V. Prohaska, C. Vermeulen and L. R. Dragstedt. *Am. J. Physiol.* 138, 264-8 (1943). The parenteral administration of lipocaic prevents the accumulation of fat in the liver produced by the injection of ketogenic hormone in fasting guinea pigs. The fatty infiltration in the liver due to fasting is also decreased by the administration of lipocaic. The Houssay animal develops the fatty liver of lipocaic deficiency just as rapidly as the depancreatized dog and is equally responsive to lipocaic therapy. Some implications of the antagonistic action of lipocaic and the anterior pituitary on fat transport are mentioned.

THE FAT-LIPOID METABOLISM IN AGED SUBJECTS. I. V. Bazilevich and L. I. Pravdina. *J. Med. Ukraine* 10, 1253-66 (1940). The fat-lipoid metabolism is distinctly altered in persons, 90-110 years old, without pathol. illnesses. Compared with normal young and middle-aged subjects, the total contents of lipoids and fat acids and all the fractions, as neutral fats, cholesterol and phosphatides, in the blood are increased in these aged subjects. (*Chem. Abs.*)

INCREASED ERYTHROCYTE DESTRUCTION ON A HIGH FAT DIET. A Loewy, L. W. Freeman, A. Marchello and V. Johnson. *Am. J. Physiol.* 138, 230-5 (1943). In 5 internal bile-fistula dogs the daily total bilirubin output was significantly higher on high fat diets than on calorically equiv. low fat diets. This effect was also demonstrated in 2 external bile-fistula dogs. These findings indicate that red blood cell destruction proceeds at a faster rate on a high fat diet than on a low fat diet; this effect is probably caused by the introduction of a hemolytic substance into the blood stream by way of the lymphatics. These sequelae of the ingestion of fat are probably 1 mechanism for normal red blood cell destruction in dogs. Calens. from the av. daily bilirubin output in this series indicate that the av. life of the red blood cell in dogs approaches 200 days.

CIRRHOSIS OF THE LIVER AMONG RATS RECEIVING DIETS POOR IN PROTEIN AND RICH IN FAT. G. T. Webster. *J. Clin. Investigation* 21, 385-92 (1942). Rats on diets low in protein and choline and rich in fat developed necrosis and cirrhosis of the liver, renal necrosis, fibrosis and hemorrhage. The liver lesions were prevented by increase in protein and addn. of molasses to the diet. The lesions were diminished by decrease of the fat and addn. of betaine. Cystine and cholesterol increased the severity of the lesions, the former being ameliorated by betaine. Generally the renal lesions were affected in the same way as liver lesions by diet changes. Neoplasms occurred in 20% of the rats receiving added cystine. (*Chem. Abs.*)

PATENTS

SHORTENING. K. R. Brown (Atlas Powder Co.). *U. S.* 2,303,432. An all purpose shortening comprises hydrogenated cottonseed oil and a small but effective amt. of a partial ester of mannitan and a fatty acid obtainable by hydrolysis of hydrogenated cottonseed oil, said mannitan ester having a (OH) no. of from 180 to 240, said shortening having a smoke point not less than about 350° F.

BLENDED EDIBLE FATS. A. Gudheim (Lever Bros. Co.). *U. S.* 2,304,452. A plastic shortening having a uniform appearance and texture in which the shortening ingredients consist essentially of 80 to 95% of an edible liquid vegetable oil and 5 to 20% of a hard fat having a titer of not less than 65°, whereby the mixt. has a plasticity at room temp. suiting it to culinary operations and retains its plasticity over a wide temp. range.

PROCESS OF TREATING WOOL GREASE. I. J. Dreker and L. I. Conrad (American Cholesterol Products, Inc.). *U. S.* 2,302,679. A process for the production of wool grease concentrates contg. free cholesterol and other alcoholic constituents only comprises the step of sapong. wool grease with an aq. medium contg. not substantially less than about 20% $Ba(OH)_2$ in

the mixt. and at a temp. not substantially exceeding 100°.

METHOD OF CONTINUOUSLY HYDROFINING FATTY ACID ESTERS. M. H. Gwynn. *U. S. 2,302,994*. A method of continuously hydrogenating fatty acid esters, comprising esters of fatty acids contg. 2 to 4 unsatns. with relatively little formation of paraffinic or isomerized esters comprises upflowing the liquid esters together with an excess of H₂ through the free space of an active black stationary Ni catalyst whose concn. is between 0.2 and 10 moles per l. and regulating the temps. so that the hydrogenation is relatively equalized in the different portions of the catalysis, particularly throughout those forward portions in which most of the hydrogenation occurs, by an ascending series of temps. above about 50°, but below about 150° and at a pressure between about 1 and 20 atms.

DEHYDRATED CASTOR OIL TREATMENT. O. A. Cherry (Glidden Co.). *U. S. 2,304,074*. The process of treating a heat bodied dehydrated castor oil having increased ac. and acid nos. due to bodying comprises extg. said heat bodied oil with a low boiling alc. of lower mol. wt. than Bu. alc.

TUNG OIL SUBSTITUTE. R. A. Swain (Interchemical Corp.). *U. S. 2,304,288*. A tung oil substitute comprises a mixt. of a product resulting from the reaction of between 1 and 3 mols. of maleic acid and 1 mol. of linseed oil and sufficient quantity of a glycerol ester of linseed fatty acids contg. free (OH) at least substantially equivalent to the acidity of the maleic acid reaction product as detd. by its acid no.

PROCESS FOR PRODUCING ALDEHYDES. J. T. Scanlan and D. Swern (Sec. of Agriculture). *U. S. 2,304,064*. The process of producing aldehydes comprises reacting an aliphatic compd. contg. 18 C atoms, an α -glycol group and an alc. group with red lead and glacial AcOH at temps. of substantially 55-65°.

TEXTILE FINISHING PROCESS. W. J. Thackston (Röhm & Haas Co.). *U. S. 2,303,773*. The process of finishing a textile fabric comprises treating said fabric with a paste comprising water, starch, a water-sol. gum, and a small amt. of a dispersion of a non-hardening, alkyd resin modified with 30 to 55% of a non-drying higher fatty acid glyceride, the amt. of starch contained in the paste being in excess of the amt. of resin dispersed therein, and drying said fabric.

TALL OIL TREATMENT. E. Segessemann (Natl. Oil Products Co.). *U. S. 2,305,498*. A process for treating tall oil to sep. fatty acids therefrom comprises hydrogenating tall oil to convert the unsatd. fatty acids into satd. fatty acids, decreasing the temp. of the resulting hydrogenated oil in the presence of a solvent therefor to effect pptn. of the fatty acids and removing the pptd. fatty acids from the remaining soln.

FATTY ACID TREATMENT. J. E. McKee and O. Grazi-
anai (Armour and Co.). *U. S. 2,304,842*. The process comprises subjecting a mixt. of fatty acids contg. unsatd. constituents to fractional distn. to produce a volatile bottom fraction contg. a hydrogenation inhibiting factor, a volatile overhead fraction contg. a hydrogenation inhibiting factor, and a volatile intermediate fraction contg. unsatd. fatty acids and subjecting the intermediate fraction to hydrogenation.

AMINO ALCOHOL ESTERS. D. W. Jayne and H. M. Day (American Cyanamide Co.). *U. S. 2,305,083*. These higher fatty acid esters of *p*-toluene sulfonic acid salts of amino alcs. have at least 1 of the radicals of the group consisting of primary amino radicals and secondary amino radicals.

AMIDE. M. Katzman (Emulsol Corp.). *U. S. 2,303,366*. A method of prepg. new chem. compds. comprises condensing monoethanolamine with the chloracetamide of monoethanolamine and then reacting the resulting compd. with a fatty acid acyl halide having at least 8 C atoms to introduce the corresponding acyl radical into the mol. in the form of an amide linkage.

QUATERNARY AMMONIUM COMPOUND AND PROCESS OF MAKING THE SAME. A. W. Baldwin and H. A. Piggott (Imperial Chemical Industries, Ltd.). *U. S. 2,303,191*. N-methyl-fat acid-amidomethyl-pyridinium chloride.

HIGH MOLECULAR WEIGHT ALIPHATIC DIAMIDE OF SEBACIC ACID AND PROCESS OF PREPARING SAME. W. O. Pool (Armour and Co.). *U. S. 2,304,475*. The process of prepg. N alkyl substituted high mol. wt. diamides of sebacic acid comprises heating a mixt. of monoamine fat acids and sebacic acid.

AMIDES OF HETEROCYCLIC CARBOXYLIC ACIDS. M. Katzman (Emulsol Corp.). *U. S. 2,304,830*. This invention relates to new chem. compds. which are, in general, amides of higher mol. wt. primary aliphatic amines with carboxylic acid derivs. of heterocyclic compds. contg. N in the ring.

WATER-REPELLENT TEXTILES AND PROCESS FOR MAKING SAME. E. Wolf (Heberlein Patent Corp.). *U. S. 2,301,352*. A permanently water-repellent cellulosic fabric having its fibers chemically treated by heating after impregnation with a compd. contg. a fat acid and comprising a tertiary amine combined with the product obtained by reacting a carbonic ester halide with hexamethylenetetramine, under conditions such that decomn. of the latter does not occur is described.

WATER-REPELLENT TEXTILE MATERIAL AND A PROCESS OF PREPARING IT. G. Balle, J. Rosenbach and L. Orthner (General Aniline & Film Corp.). *U. S. 2,301,676*. Special quaternary ammonium salts contg. a fat acid radical are used to water-proof textiles.