Deterioration of Fats and Oils

REVIEWS on the spoilage of fats and oils were contributed by K. Taufel (Angew. chem. 49, 48-53, and Z. Untersuch. Lebensm. 72, 287-99), Richard Neu (Chem.-Ztg. 60, 205-7), and I. H. Schmalfuss, H. Werner, and A. Gehrke (Fette u. Seifen 43, 211-4, 243-7).

L. H. Lampitt and N. D. Sylvester (Biochem. J. 30, 2237-49) recorded analyses of oxidized fats and correlated their findings. These results included data on the Kreis test, Issoglio value and peroxide value. The technic for the determination of peroxides by Lea’s method, and new and improved methods for the other tests, were described.

During the course of the determination of the Issoglio value, the fats lost 16 per cent of their peroxide value, about 55 per cent in intensity of the Kreis test and 55 per cent of the aldehyde value. The figures were not dependent upon the degree of oxidation of the fats. The Issoglio value appeared to be proportional to the reduction in the aldehyde value and also to the aldehyde value of the original fat. The aldehyde value and peroxide value varied in approximately direct proportion.

E. Freyer (OIL & SOAP 13, 227-9) made observations on the color changes that occurred in cottonseed oil during the stability test, which led to the development of a simplified Wheeler-Swift procedure. Just before rancidity developed in the test the oils became darker, after which they began to bleach. During the latter change rancidity became organoleptically apparent. The darkening occurred just before a peroxide value of 125 was reached, which is the adopted minimum value at which cottonseed oil is considered to be non-rancid. This characteristic was used with the new apparatus, thus eliminating the necessity of judging the end point by determining the peroxide value. The principal feature of the new apparatus is a glass bath vessel, which permits examination of the tests without removal of the tubes.

Rape seed oil, wheat germ oil, cod liver oil and oleic acid were studied by J. M. Aas (Fettchem, Umschau 43, 52-5), with a special apparatus which allowed correlations to be made between oxygen uptake, gain in weight and loss in iodine value. Wheat germ oil and oleic acid took up 3 atoms of oxygen per double bond affected. Rape seed and cod liver oils took up 2-2.2 oxygen atoms per double bond. Only 0.64 per cent volatile product was given off in 124 days of oxidation. General information on oxidative deterioration and the mechanism of antioxidants in oils were presented by E. L. Lederer (Ole, Fette, Wachse 1935 [1] 35-45). The information by G. R. Greenbank was presented graphically. The accelerating action of light was most pronounced in the presence of air followed by moisture and heat, respectively. Removal of free fat acids from butter by steam distillation followed by storage for three years under vacuum and in diffused light resulted in a negative Kreis test. M. R. Coe recorded correlations on the induction period and rancidity development between oils protected from light by a green wrapper delimiting by 4900 to 5800A and non-protected oils. The development of peroxides in the protected oils was no indication of the rate at which rancidity developed in unprotected oils. Rancidity of an oil had no necessary correlation with the development of peroxides. There was a relationship between the numerical increase in the peroxide value of an oil, previously protected from the time it was exposed to light until it became rancid, and the peroxide value of a fresh sample of the same oil when it became rancid. Robertson and Campbell studied the possible effect of storing cottonseed oil in containers made of the following commercial alloys and metals: Has-teeloy A, timmed Everdur A, Everdur A, deoxidized copper, nickle, Monel, Inconel, high-purity aluminum, commercial aluminum, Armco 18-8, Armco 17, Armco ingot iron, Allegate iron, galvanized iron and glass (enameled black to exclude light). The peroxide values of oils stored in Everdur A and deoxidized copper containers were reduced in 2 weeks from 12.8 to 4.5 with improvement in flavor, but the sample in the copper container developed rancidity in 16 weeks. The oils held in Everdur and the copper became rancid at peroxide values of 49.0 and 84.0, respectively. All the other metals reacted nearly alike. N. N. Godbole and Sadgopal tabulated results of tests on the influence of light, air, moisture content, metals and rancid ghee on the stability of Indian buffalo butter fat (ghee).

H. Schmalfuss, H. Werner and A. Gehrke (Margarin Ind. 28, 43-4; 29, 4-8) studied the effect of heat on aldehyde formation in fats. They observed that lactic acid on heating became aldehydic easier than unsaturated oils; whereas, the reverse was expected. This prompted the authors to investigate whether or not some of the aldehydes formed were decomposed on heating. Tests were made by treating oils at 120, 150 and 180° and periodically determining the aldehydes by the von Fellenberg and Kreis tests which were modified to
give some quantitative aspects. Coco fat, palm kernel fat, glycine, and paraffin oil gave good von Fellenberg tests which first increased and then decreased. Soy bean oil, peanut oil, lauric acid, methyl esters of lauric and caprylic acids acted similarly but in a lesser degree. The Kreis test was positive only in coco fat, palm kernel fat, soy bean oil and peanut oil. The intensity of the Kreis reaction rose to a maximum and then decreased. The decreases were about 100 times slower than the increases.

Several communications dealt with the action of micro-organisms on fats. J. R. Vickery (J. Council Sci. Ind. Research 9, 107-12, 196-8) tested the activity of several strains of Achromobacter, Pseudomonas and Asporogenous yeast on a synthetic medium containing 80 per cent beef fat in water-in-oil emulsion. All the strains of yeast and Pseudomonas tested were responsible for appreciable lipolysis, but only one strain of Achromobacter had this power to a slight degree. He therefore contended that the level of free acidity in beef fat does not apply generally as an index of spoilage occurring in beef fatty tissue. Where Achromobacter slim was present on stored fatty tissues, there was little lipolysis even where a heavy growth of Achromobacter existed. These investigations on antioxidants and autoxidation were reported in a series of papers by H. S. Olcott and H. A. Mattill (Oil & Soap 13, 98-100; J. Soc. Chem. Ind. 54, 1627-30, 2204-8) and L. A. Hamilton and H. S. Olcott (Oil & Soap 13, 127-9). Antioxidants for lard, derived from the unsaponifiable lipid fraction of vegetables or vegetable oils, were named inhibitors. These inhibitors can be concentrated from wheat germ or cottonseed oils by processes used for preparing vitamin E concentrates followed by further fractionating the inhibitors from the concentrated mixture. These products were transparent oils. Their activity was destroyed by reagents which attacked the hydroxyl groups or saturated ethenoid linkages, but the inactive esters could be hydrolyzed to regenerate the activity and the chlorine and bromine addition products could be reactivated with zinc and hydrochloric acid. The concentrates had a strong absorption band at 2940A, which was roughly proportional to their activity. The inhibitors were more effective antioxidants in lard than in any other compound for which use of antioxidants had been suggested. The inhibitors protected purified fat acids and esters but did not protect the vegetable oils from which they were obtained. Commercial preparations of lecithin had a moderate antioxidative action on cottonseed oil and lard and none on mixtures of lard and cod liver oil. The activity of the commercial lecithin was attributed to presence of cephalin because purified cephalin was active while purified lecithin was not. Other experiments included in this series dealt with the evaluation of several antioxidants on methyl and ethyl esters of fat acids and a preliminary classification of inhibitors. The crude methyl and ethyl esters of vegetable oil fat acids were protected to a remarkable degree by several organic dibasic acids, phosphoric acid, sulfuric acid, cephalin and some phenolic inhibitors. Hydroquinone was slightly effective and inhibitol oils were inactive. When esters were partially purified by vacuum distillation, they were only slightly protected by acids and cephalin but were protected by hydroquinone and the inhibits. They proposed a tentative classification of inhibitors into three groups: (1) acid type inhibitors; (2) inhibits and hydroquinone; and (3) other phenolic inhibitors. Hamilton and Olcott postulated that phenolic inhibitors and inhibitol induce their effect by inhibiting formation of the initial active moloxide and that they are entirely destroyed before the start of rapid oxidation. Pro-oxidants were said to decrease the period before rapid oxidative deterioration by virtue of their destruction of natural inhibitors.

A comprehensive investigation on antioxidants and preservation of edible fats was made by C. H. Lea (J. Soc. Chem. Ind. 55, 293-302T; Dept. Sci. Ind. Res. Dept. Food Investigation Board for 1934, 38-43). The oxidation of the oil in contact with water was followed by determining the peroxide oxygen content, and the results were presented in charts. The oxidation of lard in glass vessels in contact with water was much more rapid at an alkaline than at an acid pH. It was suggested that this effect was due to the production of colloidal ferric hydroxide. At pH values below 5, nitrite was found to be a powerful pro-oxidant. Copper and iron in aqueous solution accelerated the oxidation of lard; the copper was 20 times as active as iron. Iron in alkaline solution, i.e., colloidal ferric hydroxide was inactive. The various antioxidants tested were grouped according to their strength as follows: (1) Inactive—mannitol. (2) Weak—glycerol, glucose, sucrose, fructose. (3) Moderate—lactic, glycollic, and maleic acids or their sodium salts, ethanolamines and maleic acid. (4) Powerful—Polybasic hydroxy-acids and aliphatic amino-acids. The stability of oils containing the antioxidants was greatest in the presence of acids. The pro-oxidant effect of copper in concentration up to one part per million was completely inhibited by...