Report of the Literature Review Committee

Annual Review of the Literature on Fats, Oils and Detergents Part IV.

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DETERIORATION DURING STORAGE

Several attempts were made to characterize the volatile carbonyl compounds present in oxidized lipids. Methyl erucate was oxidized with air at 96C and the resulting carbonyl compounds were identified by paper chromatography and UV spectroscopy (Suzuki and Takeuchi, *Yukagaku 13*, 431). When erucic, stearic, oleic, and linoleic acids were oxidized at 180C, stearic and oleic developed more carbonyl compounds than the other two acids. The products consisted mostly of saturated and monounsaturated aldehydes, whose relative proportions varied with the initial degree of unsaturation (Hrdlicka and Pokorný, *J. Inst. Chem. Tech.* (Prague) *6*, 161). Ten economically important vegetable and animal oils were similarly oxidized. The compounds formed were analogous to those from pure fatty acids, with the addition of homologous series of C_3 to C_4 (Hrdlicka and Pokorný, *Ibid. 7*, 113) (Hrdlicka and Pokorný, *Prumysl Potravin 15*, 400). Aldehydes such as methanal, ethanal, acrolein and glyoxal were detected in seal oil aerated for 30 hr at 60–65C (Leonov and Shestakova, *Nauchn. Tr. Mosk. Tekhnol. Inst. Legkoi Prom.* No. *25*, 27). The presence of similar aldehydes, especially nonanal and hexanal, in butter was attributed to the oxidative degradation of oleic and linoleic acids, respectively (Winter et al., *J. Food Sci. 28*, 554). Butterfat oxidation products were concentrated as urea adducts and characterized. Sebacic, azelaic, *trans*- and *cis*-9,10-dihydroxystearic, 9,10-epoxystearic, 9,10-diketostearic and nonanoic acids, and azelaic semialdehyde were detected (Otake, *Rakunokagaku No Kenkyu 11*, (4) A238). The volatiles from rancid olive oil were studied spectrophotometrically. Their curves showed two maxima in correlation with the organoleptic rancidity of the oil (Foresti, *Riv. Ital. Sostanze Grasse*, (*Symposium* Issue) *1962*, 165). The oxidation products in blown linseed oil increased with the amount of air blown but the nature of the products was not affected (Premet and Lagosha, *Tr. Vses. Nauchn.-Issled. Inst. Zhirov 1963* (24) 267) (Pokorný, *J. Inst. Chem. Technol.* (Prague) *6*, 267).

Representatives of the carbonyl classes commonly detected in oxidized lipids were further oxidized at 45C. Several other carbonyl compounds resulted which were similar to those encountered in oxidizing systems but whose formation from hydroperoxide esters could not be theoretically predicted (Lillard and Day, *JAOCS 41* (8) 549) (Lillard, *Dissertation Abstr. 25* (1) 400).

The catalytic action of chelates of salicylaldehyde-ethylenediamine was qualitatively the same when applied to the oxidation of substrates with different degree of unsaturation. It varied, however, with the type of chelating metal. Chelates of Fe^{++} provoked no induction period whereas chelates of Co^{++}, Cu^{++}, and Ni^{++} did. Chelates of Zn^{++} had negative catalytic effect (Fedeli et al., *Riv. Ital. Sostanze Grasse 40*, 619). Another catalytic agent of fat autoxidation was chlorophyll, which promoted the formation of peroxides in the presence of light (Hall and Mackintosh, *J. Food Sci. 29* (4) 420).

Protection against oxidation by atmospheric oxygen could be achieved by converting fatty acids and esters to urea complexes. Esters were less protected than acids. Oleic and linoleic acids were protected whereas linolenic acid was not (Zalud et al. *Prům. Potravin 13*, 660). Increased resistance toward oxidation was obtained when linoleic acid was mixed with amino acids such as arginine and lysine (Chang and Linn, *JAOCS 41* (11) 780). Cystein proved to be a powerful inhibitor of oxidation in lard, having synergistic behavior in mixtures with glycine. Similar effects were shown by extracted soybean meal and, to a smaller degree by casein and albumin (Pokorný et al. *J. Inst. Chem. Tech.* (Prague) *5*, (3) 161). Proteidic substances from hide parings also had a retarding effect on the oxidation of unsaturated fatty acids. In comparison to native lipids, however, added lipids uniformly distributed through the proteidic material were less protected against oxidation (Pokorný et al., *Ibid., 6*, 185; *Ibid.* 195; *Ibid.* 207). In fact, after different treatment, proteidic materials could promote oxidation (Pokorný et al., *Ibid., 6*, 153) (Dluzewska, *Zeszyty Nauk. Szkoly Glownej Gospodarst Wiejskiego Warszawie, Rolnictwo No. 4*, 247). Thermally abused corn oil could form complexes with egg albumin. Polymerized oil was less reactive than oxidized oil. Keto and epoxy groups had more influence on complex formation than hydroxy and hydroperoxide groups (Narayan et al., *JAOCS 41*, 254), see also (Matsuo, *Eiyo To Shokuryo 16*, 260).

The rancidity of 23 different kinds of fats and oils used commonly as foods was measured. Boiled sardines, smoked squid, hams, and shirasu-tsukudani were the most readily oxidized. Fried peas, broad beans, peanut butter, doughnuts and butter cookies were less sensitive. Lard, butter and margarine were the most resistant (Kajimoto et al., *Shokuhin Eiseigaku Zasshi 4*, (6), 358). When margarine, lard and shortening were compared after storage at 30C, very little change was noted in lard and shortening, but margarine showed decreased iodine and thiocyanogen values as well as decoloration (Niiya and Yamamoto, *Ibid. 5* (1) 33) (*Ibid. 5* (2) 130). In general, the rate of autoxidation in packaged foods depended on the partial pressure of oxygen, whereas the degree of autoxidation depended on the amount of oxygen present (Heiss and Radtke, *Verpackungs-Rundschau 13*, (6) 45).

Several vegetable oils were examined for their content of oxidation products. In one case, when virgin and refined olive oils were mixed in different proportions the stability of the mixtures was not directly related to the stabilities of the original oils (Borbolla v Alcala and Vazquez-Ladrono, *Grasas y Aceites 14*, 254).

The reversion of edible oils (Debruyne, *Rev. Franç. Corps Gras 11* (1) 13) or in particular that of oils containing linoleic acid (Holm, *Acta Polytechn. Scand.* (Chem. Series No. 21) (1963) *Norw. Contr.* (16) 48) was discussed. The darkening in color of vegetable oils during hydrogenation could be attributed to its Ni content, since very little Fe and Cu were present and a good correlation could be established between Ni content and color intensity (Pokorný et al., *J. Inst. Chem. Tech.* (Prague) *5* (1) 203), see also (Catalano, *Ann. Fac. Agrar., Univ. Bari 17*, 369).

Changes induced by processing operations could affect oil stability. Those caused in soybean oil by neutralization, bleaching, deodorization and storage were discussed (Vargas Romero, *Rev. Franç. Corps Gras 11* (1) 3). Heat treatment of rice bran oil prior to extraction and refining decreased its keeping quality. Free fatty acids added to refined fresh or preheated oil also decreased keeping quality but more in fresh than in preheated oil. Addition of antioxidants increased stability but the relative effectiveness of the antioxidants tested did not follow the same order in the different oils treated. Deodorization decreased the stability of fresh oil, even in the presence of antioxidants. Hydrogenation could increase the stability of an oil up to 50% (Chahine and Radwan, *Grasas y Aceites 15* (3) 129). Hydrogenation of rapeseed oil was shown to proceed selectively. Acids of two to three double bonds were hardened almost exclusively while small amounts of saturated acids were formed. *Cis-trans* isomerization occurred, prevailing over a hydrogen addition (Pokorný and Ruzicka, *Prumysl Potravin 15*, 392). The hydrogenation rate depended on the position of the double bond, i.e., the distance from the carboxyl group, rather than on molecular weight (Kosman, *Ibid., 15*, 394) Jakubowski, *Ibid. 15*, 397).

Heating of methyl linoleate with bleaching earths in the absence of air caused no conjugation when the temperature was 100C or less but at 200C some bleaching earths produced conjugation. True isomerization was observed only above 150C (Ney, *Fette Seifen Anstrichmittel 66* (7) 512). Earth bleaching was replaced by a treatment with alumina in the refining of peanut oil. The material adsorbed on the alumina was rich in oxidized, hydroxylated and unsaponifiable material (Crossley and Thomas, *JAOCS 41* (2) 95).

Oils extracted in the presence of proteolytic enzymes and ascorbic acid proved to be less sensitive to oxidative alteration, especially upon exposure to light (Garoglio and Stella, *Olearia 17*, 5). The deterioration of cottonseed oil heated in the presence of phosphatides and gossypol (Sterlin and Burnasheva, *Tr. Vses Nauchn.-Issled. Inst. Zhirov 1963* (23) 230) and the decomposition of carotene in stored clover meals (Walger et al., *Agrokem. Talajtan 12* (3) 391) were also investigated.

Olive oil samples were added 0.1% of either alcohol or glycerol and stored for a year. The addition of alcohol had no effect but the addition of glycerol retarded the acidification by 10% as compared to control samples (Fahmy, *Agr. Res. Rev.* (Cairo) *41* (4) 61). During the first few days after expression of the oil, olive husks underwent a lypolytic process which proceeded linearly with time (Carrante and Tricarico, *Riv. Ital. Sostanze Grasse, Sympos. Issue 1962*, 109). Enzyme hydrolysis was also the main cause for the deterioration of stored rapeseed and its diminished keeping quality. However, the lipolytic processes were related in no simple way to the decrease in stability. Freezing of the seeds or storage at 40C in the presence of water lowered oil quality, whereas storage at 2 to 20C gave optimum results (Janiček and Pokorný, *J. Inst. Chem. Tech.* (Prague), *7* (2) 173).

Differences in both the proportions of the various lipid classes and the fatty acid composition were found in rice kept at either 9C or room temperature (Yasumatsu and Morita, *Agric. Biol. Chem. 28* (5) 257). The increase in free fatty acids upon storage induced an increase in viscosity (Yasumatsu et al., *Agric. Biol. Chem. 28* (4) 265). The liberation of fatty acids in wheat flours was followed for up to 476 weeks. The free fatty acid augmented with time (Morrison, *J. Sci. Food Agr. 14*, 870). Corn was stored for long periods of time and its lipase activity was determined at various relative humidities. Lipase caused hydrolysis or synthesis of glycerides depending on storage temperature (Makarov and Prokhorova, *Tr. Vses. Nauchn.-Issled. Inst. Zerna i Produktov ego Pererabotki 1963* (43) 57. In germinating corn, lipase activity grew with time. Since also the saponification number increased, accumulation of products of low molecular weight was adduced (Lavrishcheva and Mal'tsev, *Izv. Vysshikh Uchebn. Zavedenii, Pishchevaya Tekhnol 1964* (3) 104).

The fermentation of vegetables caused a rise in the free fatty acid content of their neutral lipid fraction. Inversely, the free fatty acid fraction of the acetone-soluble and acetone-insoluble fractions decreased, as did the unsaponifiable matter (Vorbeck et al., *J. Food Sci., 28*, 495) (Pederson et al., Appl. Microbiol. *12* (6) 513). Breakdown of phospholipids was observed in baker's yeast during drying (Harrison and Trevelyan, *Nature 200*, 1189). An emulsion of soybean oil, egg phosphatides, and glycerol in water showed a linear increase in the free fatty acid content with respect to the time of storage (Boberg and Hakansson, *J. Pharm. Pharmacol. 16* (10) 641).

The problem of oxidative rancidity in meat and meat products was reviewed (Sulzbacher et al., *Proc. Res. Conf. Res. Council Am. Meat Inst. Found. Univ. Chicago, 15*, 111). Animal fats with high initial peroxide contents deteriorated on storage at a faster rate than fats with lower peroxide values (Bernatoniene et al., *Lietuvos TSR Aukstuju Mokyklu Mosklo Darbai, Chem. ir Chem. Technol. 5*, 145). The process of lipid oxidation was followed in cured and uncured samples of cooked pork. The alterations in the uncured samples might be attributed to hem-catalyzed oxidation during preparation for freezing and thawing. Instead, the cured samples underwent salt-catalyzed oxidation during frozen storage (Zipser et al., *J. Agr. Food Chem. 12* (2) 105). The addition of Cu to autoxidizing lard lowered its peroxide value due to the metal's catalytic activity on peroxide decomposition (Pokorný and Janiček, *J. Inst. Chem. Tech.* (Prague) *7* (2) 183).

In animal fats kept at 15 and 0C, the greater alterations were due to bacterial activity (Ostric-Matijasevic, *Technol. Mesa 3* (4) 5). The activity of microbial lipases in stored meat was assayed and the released fatty acids studied by gas-liquid chromatography. Elevated temperatures and aeration reversibly inhibited lipase action. Lipases from different microorganisms were not alike although some overlapping of specificities existed (Alford et al., *Proc. Res. Conf. Advisory Council Res. Am. Meat Inst. Found. Univ. Chicago 15*, 11). Beef tallow containing 0.08–3.60% water was stored for 200 days at 600C. The amounts of fatty acids and glycerol released were directly related to the amount of water originally present (Crespo et al., *Rev. Arg. Grasas y Aceites (Buenos Aires) 5*, 48). Sheep fat was kept at −2C, −8C, and at room temperature for 540 days. After chemical and organoleptic examinations the samples stored at −2 and −8C were found acceptable for human consumption (Nakonechnyi, *Myasn. Industr. SSSR 33*, (5) 54). Fat from geese, ducks, or turkeys rendered at 60C or stored at 4C could be kept 1 to 4 months longer than samples rendered or stored at higher temperatures (Grabowski, *Roczniki Technol. Chem. Zywnosci 10*, 77). Unpacked dehydrated chicken showed a significant increase in acid and peroxide numbers after prolonged storage at approximately 20C (Ishukov et al., *Tr. Tsentr. Nauchn.-Issled. Inst. Ptitsepererabat. Prom. 9*, (18). Samples of turkey kept at 4C for one week showed significant differences in their rates of lipid autoxidation. A noticeable delay in oxidation was achieved by the addition of egg albumen solids, BHA, or phosphates (Marion and Forsythe, *J. Food Sci. 29* (5) 530).

Two rates of hydrolysis were observed in frozen cod phospholipids; the slower rate occurring at the beginning. The lag could be eliminated by either very fast or very slow freezing followed by thawing, but not by freezing at an intermediate rate (Lovern and Olley, *J. Food Sci. 27*, 551). Herring oils of iodine values 192 and 130 were compared for their resistance towards oxidation. The more unsaturated oil was found more resistant (Astrup, *Chem. Ind.* (London) *1964*, 107). Herring and mackerel fillets were stored in bags at −20 and −30C and the effects of various treatments against oxidative rancidity were tested (Liljemark, *Food Technol. 18* (3) 122). When sun-dried mackerel muscle slices were packed in polyethylene bags under vacuum or in air or nitrogen atmosphere and stored at 5–12C for 30 days, no clear cut differences were detected (Oyama, *Kagoshima Daigaku Suisan Gakubu Kiyo 12*, 7). Rancidity developed more rapidly in gutted than in whole iced trout (Hansen, *J. Sci. Food Agr. 14* (11) 781). In the gutted sample the limiting factor with relation to their keeping quality was the development of rancidity in the surface fats of the belly wall (Hansen, *J. Sci. Food Agr. 15* (5) 344).

The iodine number of sardine oil varied according to the method of extraction. Extraction at room temperature with protection from air provided oils with iodine numbers up to 40 units higher than oils extracted by methods involving heating (Lopez Costa, *Bol. Inst. Españ. Oceanog.* No. *115*, 12pp).

Selective hydrogenation of fish oils increased their stability.

No difference was found between catalysis of the hydrogenation reaction by Ni alone or by Ni and dimethyl polysiloxane (Shimamura et al., *Yukagaku 13*, 365).

A low density, insoluble material of lipid character was found in dogfish tissue extracts which increased markedly the protein stability. This suggested the existence of some relation *in situ* between lipid hydrolysis and protein denaturation in stored fish muscle (Anderson and Steinberg, *J. Food Sci. 29* (3) 327).

In freeze-dehydrated jack mackerel preserved at 37C, the thiobarbituric acid (TBA), unsaturated carbonyl, and peroxide values changed markedly in a relatively short time. This oxidation of the lipid moiety of the muscle was associated with protein denaturation (Toyomizu et al. *Nippon Suisan Gakkaishi 29*, 854) (Toyomizu et al., *Ibid. 29*, 1037).

Shipe discussed the factors involved in the development of oxidized flavor in milk (*J. Dairy Sci. 47* (2) 221). Milk phospholipids were examined for their degree of oxidation at various pH's. Phosphatidylethanolamine showed maximum oxidation between pH 2 and 4, whereas phosphatidyl choline and phosphatidyl serine had their maxima between pH 2 and 6 (Mattson and Swartling, *Milk Dairy Res.* (Alnarp.), Rept. No. 68, 23 pp.).

Important factors in the stability of milk fat during storage were its total content of readily oxidizable conjugated acids and of tocopherol (Zalashko, *Izv. Vysshikh Uchebn. Zavedenii, Pishchevaya Teknol. 1960* (3) 18). The level of polyunsaturated fatty acids in milk was not affected by normal manufacturing conditions. However, changes were observed occasionally under storage conditions which permitted microbial growth (Boatman and Hammond, *J. Dairy Sci. 47* (2) 194). Oct-1-en-3-one, probably coming from linoleic acid, accounted for metallic flavor in autoxidized milk. Greasy flavor was associated with the presence of *trans-cis*-2, 6-nonadienal, probably formed from linolenic acid (Hammond and Hill, *JAOCS 41* (3) 180).

The interrelations among phospholipid content, fatty acid composition, and milk fat hydrolysis were studied (Wallace, *Dissert. Abstr. 24* (12) 4974). Treatments such as homogenization, agitation, and temperature fluctuations could liberate milk lipase from its association with the casein micelle. Prompt cooling activated the liberated enzyme, which subsequently attacked the fat globule. As a result, milk flavor and odor might be altered and the surface and interfacial properties modified (Jensen, *J. Dairy Sci. 47* (2) 210). Milk lipase activity was maximum near pH 9 (Stadhouders and Mulder, *Neth. Milk Dairy J. 18*, 30). There was no relation between the susceptibility of milk to lipolysis and the source of nutrients or the nutritional level of the cows (Cannon and Rollins, *J. Dairy Sci. 47*, 41). Estrus was not an important factor either (Dunkley et al., *Ibid. 47* (7) 818).

Only a slight increase in acidity was noted in cheese butterfat after 12-month storage (McDowell, *J. Dairy Res. 30*, 369). The increase could be slowed by the addition of 0.03 or 0.01% of hydrogen peroxide (Pijanowski et al., *Zeszyty Nauk. Szkoly Glownej Gospodarst. Wiejskiego Warszawie, Rolnictwo* No. 4, 295).

The tocopherol content of milk fractions was three times higher in the fat globule membrane than inside the fat globule. During lipid oxidation, tocopherol decrease in the membrane was more marked than that inside the globule (Erikson et al., *J. Food Sci. 29* (1) 269).

The problems associated with the nutritional use of oxidized oils and fats were reviewed (Glavind, *Dansk Kemi 44* (2) 19) (Kaneda, *Yukagaku 12*, 541) (Kaneka et al., *Yukagaku 12*, 568). Peroxides accumulated in the livers and kidneys of rats fed sunflower oil of high peroxide content (Parteshko, *Vopr. Pitaniya 23* (5) 20). Oxidized beef fat seemed to exert, when fed to rats, a depressant effect on the absorption or deposition of dietary linoleate (Lea et al., *Brit. J. Nutr. 18* (3) 369). Differences in the nutritional value of brown and white fish meals could be correlated to their content of oxidized lipids (Saruya et al., *Nippon Suisan Gakkaishi 29*, 948) (*Ibid.* 953). Oxidized cod-liver oil lipids apparently induced blockade of the reticuloendothelial system when fed to rats (McKay et al., *Lab. Invest. 13* (1) 54). The nutritional values of herring meal with or without added antioxidants, solvent extracted herring meal, cod-liver oil, and dried milk were compared (Astrup et al., *Rappt. Nord. Fettharskningssymp.* 3, Sandefjord, Norway *1961*, 204 (Pub. 1962).

Epoxidized soybean oil was fed to rats. A daily dose of 45 mg caused the death of 80% of the animals in 8 days. Doses of 5 mg/day inhibited growth, lowered dietary protein efficiency and blood cholesterol level, and increased water consumption and total blood lipids and phosphatides. Accumulation of epoxy acids on body fats could also be observed (Kieckebusch, *Fette Seifen Anstrichmittel 65*, 919). In another experiment, oxidized soybean oil was hydrolyzed and the resulting hydroxylated oil was also fed. Growth inhibition, impairment of liver function, and rise of blood cholesterol and total lipids resulted (Lang et al., *Helv. Physiol. Pharmacol. Acta 21*, 354).

Growth inhibition caused by oxidized oil feeding could be prevented by the addition of pyridoxine to the diet at a level of 250 gamma/day/50 g body weight (Kojimoto, *Eiyogaku Zasshi 21* (2) 32). The addition of 12-oxo-*cis*-9-octadecenoic acid to diets at room temperature over prolonged periods of time induced lipid autoxidation. Chickens fed the altered mixture developed symptoms of encephalomalacia (Kokatnur et al., *Indian J. Exptl. Biol. 1*, 190).

The most common methods for the evaluation of fat stability were submitted to a comparative study. The results indicated that none of the methods tested could be used as an index of shelf stability. The most reliable appeared to be the modified ASTM oxygen bomb method (Pohle et al., *JAOCS 41* (12) 795). The TBA method focussed considerable attention. The chemical characteristics of the reaction were investigated (Tarladgis et al., *J. Sci. Food Agric. 15* (9) 602) Wills, *Biochim. Biophys. Acta 84* (4) 475) (Yu and Sinnhuber, *JAOCS 41* (8) 540), and several applications were described (Inoue and Kihara, *Kaseigaku Zasshi 14*, (5) 330) (Jacobson et al., *JAOCS 41*, 124) (Keskinel et al., *Food. Technol. 18*, 101) (Mihelic, *Kem. Ind.* (Zagreb) *12* (3) 147) (Saslaw et al., *Nature 200*, 1098) (Torres and Granger, *Rev. Port. Farm. 13* (4) 463) (Munker, *Fischereiforschung 5* (6) 25). The method was compared with the peroxide value methods (Pohle et al., *JAOCS 41* (10) 649).

A procedure for the determination of malonaldehyde by UV spectrophotometry was developed (Kwon and Watts, *J. Food Sci. 28*, 627) (Kwon and Watts, *Ibid. 29* (3) 294) (Kwon, *Dissert. Abstr. 24* (11) 4623).

The common procedures for the estimation of the peroxide value were investigated (Lea and Parr, *Chem. Ind.* (London) *1964* (36) 1560), compared with other methods (Montefredine and Testa, *Riv. Ital. Sostanze Grasse, Symp. Issue 1962*, 169) (Tananger, *Rappt Nord. Fettharskninkssymp.* 3, Sandefjord, Norway, *1961*, 124 (Pub. 1962)) (Lyubavina, *Rybn. Khoz. 40* (6) 75) (see also (Pohle et al., *JAOCS 41* (10) 649) above) and tested for new applications (Pokorný et al., *J. Inst. Chem. Technol.* (Prague) *6*, 291). Factors for the interconversion of peroxide values determined by different methods were given (Rutkowski, *Przemyl Spozywczy 15* (2) 20).

The evaluation of carbonyl compounds in oxidized fat was another means of measuring rancidity (Gaddis et al., *J. Food Sci. 29*, 6) (Horwood and Williams, *Spectrochim. Acta 19*, 1351) (Jordan and Veatch, *Anal. Chem. 36*, 120) (Lea and Jackson, *Chem. Ind.* (London) *1964*, 1429) (Lyubavina, *Rybn. Khoz. 40* 51) (Schwartz et al., *Anal. Chem. 35*, 2191). Several other methods for the estimation of rancidity were proposed or modified (Ivanov, *Maslob. Zhir. Prom. 30* (6) 13) (Petruccioli, *Olearia 17*, 187) (Esterbauer and Schauenstein, *Monatsh 94*, 998) (Mroczkowski and Ossowska, *Prace. Inst. Lab. Badawczych Przemyslu Spozywczego 11* (3) 1) (Ramsey and Kemp, *J. Food Sci., 28*, 562) (Ramsey et al., *Food Technol. 18*, 105). Furthermore, procedures were tested for the determination of oxidized acids in olive oil (Naudet, *Oléagineaux 19*, 449) and of fat acidity in corn (Joffe and Small, *Cereal Chem. 41* (4) 230). A method for the synthesis of expoxy plasticizers from esters of tall oil fatty acids and methyl oleate was developed (Plochocka, *Przemysl Chem. 43* (9) 490).

Patents were issued for procedures to enhance the stability of granular or powdered lecithin (*Japan 3043* (1964), of emulsions of edible fats and oils (*Fr. 1,350,431*) and of epoxidized oil (*U.S. 3,150,153*). Several procedures for the preparation of epoxy compounds (*Japan 20,309*) (*U.S. 3,112,-325*) (*Fr. 1,338,890*) (*Belg. 634,507*), or for making resins from them (*Japan 22,744*) (*Japan 26,572*) (*Japan 6657*) (*Japan 20,992*) (*U.S. 3,148,199*) (*Brit. 953,422*) (*U.S. 3,129,-231*) were patented. A support with added Pt, Ru, or Pd was used to decompose peroxides in autoxidized fatty acids (*Fr. 1,334,673*).

DETERIORATION BY HEAT

The changes caused by heating operations on fatty materials were discussed (Blasi, *Lipidos 23*, 40, 85). The polymerization of drying oils was also a matter for discussion (Wexler, *Chem. Revs. 64* (6) 591). Several pure compounds were thermally abused and the alterations characterized. Trilinolein was heated at 200C for 5–9 hr. The tendency in the change of constants was about the same as those in common vegetable oils. The concentration of monomers decreased with time of heating, while dimers increased (Ota et al., *Yakugaku, 13*, 264). Tristearin was heated and the resulting products studied

by the derivatographic method. Stearic anhydride and its decarboxylation product, diheptadecylketone were found, together with stearoyl-epihydrin and its decomposition products, stearic acid and acrolein (Lorant and Boros, *Seifen-Oele-Fette-Wachse 90* (13) 392).

Linseed oil methyl esters were autoxidized at 40C by bubbling air through. As a consequence, ethylenic linkages decreased, *cis*-double bonds were converted into *trans*- and conjugated double bonds, and hydroperoxides were formed. The autoxidized samples were further heated for 1 hour at 200C. The hydroperoxides decomposed while polyenes started to form. The samples previously heated at 200C were then heated at 300C. The content of hydroxyl-compounds decreased while polymers increased. Very little residual conjugated double bonds were detected, whereas *trans*-isolated double bonds increased. Heating at 400–500C caused the formation of cleavage products of low molecular weight and more polymerization, while hydroperoxides and double bonds decreased (Izumi and Yamada, *Yukagaku 13,* 418) see also (Mayne and Ramshaw, *J. Appl. Chem.* (London) *13* (12) 553).

The modifications induced in the oil by thermal abuse under common commercial conditions were examined. Partially hydrogenated lard was heated at 190C for 48 hours, both in the presence of air and under nitrogen atmosphere. Viscosity, titratable acidity, iodine number, and peroxide value changed radically in the presence of air but not under nitrogen. The rate of change of these indexes was directly proportional to the degree of exposure of the fat to oxygen (Rock and Roth, *JAOCS 41* (3) 228) and inversely proportional to the temperature of the heating element (Rock and Roth, *JAOCS 41* (8) 531). When lard was heated, its stability changed, its biological value was reduced, and undesirable cleavage products developed (Ondreicka et al., *Vopr. Pitaniya 22* (6) 43). In another experiment, 12 different fats and oils were heated at 180C for 6–10 hr. The viscosity and iodine and hydroxyl numbers increased but the epoxide number remained unchanged. The amount of polymerized material was in proportion to the concentration of hydroxy acids, and this to the original degree of unsaturation of the oil (Becker and Rost, *Fette Seifen Anstrichmittel 66,* 123). In thermally treated soybean oil the iodine number was decreased while the acid and saponification values, refractive index, and the conjugate diene content increased. No changes were observed in the trichlorobenzoic acid, carbonyl, and peroxide values (Uezumi et al., *Eiyo To Shokuryo 15* (3) 15). Corn oil triglycerides were thermally oxidized at 200C. After 48 hours, about 62% of the original oil remained unchanged, the rest being polymeric and degraded products of low molecular weight (Sahasrabudhe and Farn, *JAOCS 41,* 264). In general, it was concluded that during the thermal oxidation of fats, the following events occurred: formation of oxidation products in excess of their own degradation products; eventual decomposition of hydroperoxides to aldehydes and other substances with free carbonyl groups; polymerization (Sedlacek, *Nahrung 8* (1) 58).

The chief factors that govern the loss of oil during deep frying, namely time of cooking, frying temperature, and composition of the food were investigated. No significant differences were found among soybean, cottonseed, and rapeseed oils in the degree to which they were absorbed by the fried food. On the other hand, significant loss differences were caused by diverse temperatures of frying. Finally, loss of oil increased with time (Ota and Izuyama, *Yukagaku 13,* 328).

An extended series of papers described the changes in fats and related materials induced by frying procedures. Some of the topics covered were the influence of rancid oil on cooking (Kajimoto, *Eiyo To Shokuryo 12,* 385); decomposition of antioxidants by heat (*Ibid. 13,* 82); detection of antioxidants (*Ibid. 13,* 246); antioxidant properties of smoke components (*Ibid. 13,* 250); decomposition of chlorophyll (*Ibid. 13,* 313; *16,* 56 and 60) and vitamin C (*Ibid. 13,* 317) in vegetables by frying in rancid oils; effect of antioxidants on bacteria (*Ibid. 14,* 118, 331, 371, and 384), on fungi (*Ibid. 14,* 378) and on the browning of smoked foods (*Ibid. 14,* 122); the denaturation of proteins (*Ibid. 14,* 467) and loss of minerals (*Ibid. 14,* 221) in whale meat fried with rancid oil; deterioration and coloring of the frying oil (*Ibid. 14,* 382). A correlation was established between the peroxide value of a frying oil and the extent of foaming (Kajimoto and Mukai, *Eiyo To Shokuryo 16* (5) 425), and between the degree of foaming and the nutritional properties of the oil (Kajimoto et al., *Ibid.* 432). The degree of foaming was also compared to changes in the fried material (Kajimoto, *Ibid. 16* (6) 506). The influence of the fried material on the development of rancidity by the oil was explored (Kajimoto and Kamo, *Ibid.* 510).

Potato slices were fried in three previously abused oils and the oils analyzed. The acidity increased and the saponification numbers slightly so, whereas the iodine values decreased. No polymer formation was detected. The most marked effects were seen in the absorbance spectra (Montefredine, *Atti. Conv. Intern. Lipidi Aliment. Simp. Genuinita Oli. Aliment, 3°, Rimini* (Italy) *1962,* 657 (Pub. 1963)). Soybean oil, olive oil and 2 mixtures of the two were used in the deep-frying of potatoes. Frying increased the density, viscosity, and acidity of the oil used for frying but not of that extracted from the fried food (Monteoliva et al., *Anales Bromatol.* (Madrid) *15* (3) 255), see also (Strock, *Dissert. Abstr. 24,* 2861). Cottonseed oil and lard used to fry either chicken or potatoes were analyzed for their fatty acid composition. The linoleic acid content of cottonseed oil decreased from 57 to 49% upon use. The linoleic acid in lard decreased when potatoes were fried but not with chicken. The fatty acid composition of the fat extracted from fried chicken was affected by the fatty acid composition of both the frying oil and the chicken itself (Kilgore and Luker, *JAOCS 41* (7) 496).

Fresh corn oil and the same oil after being heated at 178C in the presence of air were submitted to lipase hydrolysis *in vitro.* The thermooxidative treatment moderately decreased the susceptibility of the oil to enzymatic hydrolysis (Rinetti and Giovetti, *Minerva Dietol. 3,* (4) 172).

The effects of heat on the lipids of sunflower seeds (Kopeikovskii and Kostenko, *Biokhim. Zecna i Khlebopecheniya No. 7,* 233) (Romanova and Sazykina, *Tr. Vses. Nauchn.-Issled Inst. Zhirov No. 22,* 26), fish meal (Mason and Weidner, *Acta Agr. Scand. 14* (1) 87), oat flakes (Pokorný et al., *J. Inst. Chem. Tech.* (Prague) *7,* (2) 285), and coffee beans (Kaufman and Schickel, *Fette Seifen Anstrichmittel 65,* 1012) were also characterized. A fraction consisting primarily of unsaturated fatty acids was found responsible for the heat sensitivity of wool wax (Anderson and Poulter, *J. Textile Inst. 55* (7) T345). The changes induced by heat in olive oil could be better characterized spectrophotometrically (Ferranti, *Sci. Tech. 4* (4) 198).

Hanson compiled communications presented at a symposium on Chemical and Nutritional Aspects of Oxidized and Heated Fats. The topics discussed included the chemical effects of heating and its nutritional consequences, hydroperoxide metabolism, influence of hydroperoxides on mitochondrial function, etc. (*Chem. Ind.* (London) *1964* (36) 1541).

Commercially obtained fats were heated at 182C for 120 hr and fed to rats. After a year, weight gains and food intake were either not significantly or only slightly different from those of the animals fed fresh oil (Poling and Rice, *Fed. Proc. 23,* 552). The digestibilities of corn oil and vegetable oil shortenings were not affected substantially by heating but those of cottonseed oil and lard were reduced (Rice and Poling, *Fed. Proc. 23,* 552).

Oils heated at 200C in a CO_2 atmosphere for up to 200 hr were compared in their nutritional effects with oils with peroxide numbers of 100, 200, and 300. The effects were more pronounced with the peroxidized oils than with the heated ones (Hashimoto, *Eiyogaku Zasshi 18* (6) 375). Feeding of heat-treated (325C under inert atmosphere) anchovy oil has consequences which varied with the dietary level. Feeding of 20% altered oil caused diarrhea, weight loss and low survival. Less severe symptoms were noted with a 10% level. At a 5% level growth was normal. The symptoms provoked by the anchovy oil were more marked than those caused by other commercial oils similarly treated (Burroughs et al., *Fed. Proc. 23,* 551). Peanut oil (Kokatnur et al., *Indian J. Biochem. 1* (2) 106) and coconut meal (Butterworth and Fox, *Brit. J. Nutr. 17,* 445) were also tested for the damage caused by heating on their nutritive value. Several thermally abused vegetable and animal fats were shown to cause tissue damage when fed (Simko et al., *Nutritio et Dieta 6,* (2) 91). Others had carcinogenic effect (Arffman, *Acta Pathol. Microbiol. Scand. 61* (2) 161).

The oral administration to rats of dimeric fatty acids at a 5% level provoked toxic reactions (Czok et al., *Z. Ernaehrungswiss 5* (2) 80). A small part of the dimeric acids became incorporated (Fricker et al., *Ibid. 5,* 57).

Heating could also cause the deterioration of the lipid-l-soluble vitamin content of various products, such as milk (Agrawal and Singh, *Vidyapeeth 2,* 26), fish liver oils (Baba, *Eiyogaku Zasshi 21* (1) 3) and vegetables (Booth and Bradford, *Intern. Z. Vitaminforsch. 33,* 276).

Methods were developed for the evaluation of the stability of frying oils (Kumazawa, *Yukagaku 13,* 288), the polymerization activity of linseed oil (Pokorný, *J. Inst. Chem. Tech.* (Prague) *5* (3) 51) and for determining the molecular weight of thermal polymers by the isopiestic method (Fedeli et al., *Chim. Ind.* (Milan) *45* (2) 208) or by GLC of their pyrolysis products (Braun, *Farbe Lack, 69,* 820).

Patents were issued for the dimerization of fatty acids (*Belg. 634,034*), for the obtaining of elastic polyester resins from thermal polymers (*Pol. 47,941*), and for the preparation of a fat product which improved margarine frying quality (*Ger. 1,167,637*).

DETERIORATION UPON IRRADIATION

The deterioration of fat by irradiation was tested in simplified systems. In one experiment, methyl myristate was irradiated both under vacuum and under oxygen. Irradiation under vacuum caused the accumulation of peroxides, carbonyl compounds, and reducing substances. In the presence of oxygen, peroxides and carbonyl compounds were formed. Similar treatment of methyl linoleate under vacuum resulted in the destruction of pre-formed hydroperoxides. Antioxidants had relatively little effect in retarding peroxide formation (Chipault and Mizuno, *JAOCS 41* (7) 468). Electron spin resonance spectroscopy was found helpful in the study of gamma-ray-induced changes in triglycerides and fatty esters (Lueck et al., *Fette Seifen Anstrichmittel 66*, 249). Air dried films of neutral fats, oleic acid, and phospholipids were irradiated with gamma-rays. Increased peroxides were found in neutral fats and oleic acid (Gromov et al., *Radiobiologiya 4* (3) 378).

Some natural fats and oils were tested. Cod-liver oil was irradiated in sealed ampules with 1.5×10^6r of gamma rays. An increase in the content of saturated fatty acids was observed and attributed to the reduction of oleic, linoleic, and clupanodonic acids. The presence of 0.01% dodecyl gallate markedly suppressed the reduction process (Fomin, *Tr. Tsentr. Inst. Usoversh. Vrachei 1962*, 143). From fish-lipid fatty acids, methyl docosahexenoate was isolated, purified, and irradiated *in vacuo*. No gross alterations were observed (Stout, *U.S. At. Energy Comm. TID-18657*, 19 pp.). Twenty-four samples of food fats were submitted to irradiation with gamma rays. As a result the peroxide acid numbers increased, as did the amount of epihydrinaldehyde. Degradation and saturation of double bonds also occurred (Fomin, *Materialy Resp. Itog, Nauchn. Konf. po Gigiene, Leningrad, Sb. 1963*, 158). Irradiation of rice bran could not inhibit the enzymatic hydrolysis of its oil (Diaz et al., *Rev. Arg. Grasas y Aceites* (Buenos Aires) *5*, 57).

The influence of the intramuscular fat level on the organoleptic, physical, and chemical properties of irradiated pork was investigated. Two pre-irradiation treatments, heating at high temperatures for short periods of time or at low temperature for long periods, were compared (Whitehair et al., *Food Technol. 18*, 108) (*Ibid.* 114). Irradiation of milk fat *in vacuo* induced the formation of carbonyl compounds. These compounds were isolated and analyzed. Alkanals were most abundant, from C_{16} to C_1 in decreasing proportions. Also methyl ketones, especially of 4, 5, 7, 9, 11, and 15 carbons were detected. Most probably, long-chain aldehydes and methyl ketones were produced via hydrolytic rather than oxidative processes (Day and Papaioannu, *J. Dairy Sci. 46*, 1201).

The content of lipoproteins of egg yolk decreased upon irradiation from Co^{60}. Acid, saponification, and iodine values were not affected markedly (Nonami and Takeuchi, *Nippon Nogeikagaku Kaishi 36* (4) 301). Soybean oil, previously irradiated with 10 megarads or more, was fed to rats for 3 to 6 months. High mortality resulted. Liver function was altered, the livers and spleens showing deposition of a brown pigment. Other symptoms were inactivation of the thyroid with consequent lowering of body temperature and basal metabolism (Lang, *Z. Ernaehrungswiss. 2*, 141).

UV irradiation of lard, cacao butter, beef tallow and linseed oil at low temperature caused the development of free radicals, as indicated by their electron spin resonance spectra. These radicals had a shorter life than those formed upon irradiation with gamma rays (Deffner et al., *Z. Lebensm. Untersuch.-Forsch. 125* (4) 281).

LIPOXIDASE OXIDATION

The present knowledge on properties and function of the lipoxidase of soybean seeds was reviewed (Andre, *Oléagineaux 19* (7) 461). Oils extracted from soybean seeds from fresh soybean curd preparation and from the same dried at 40C, showed differences in iodine, acetyl, saponification, and acid numbers and in density which could be ascribed to the presence of lipoxidase. When fatty acids of soybean oil were submitted to lipoxidase action, low molecular weight acids and hydroxy acids resulted (Andre and Hou, *Oléagineaux 19* (3) 187). Some unidentified bacteria isolated from garbage showed lipoxidase activity on soybean oil which turned viscous and brown in their presence. The lipoxidase extracted from bacterial cells had an optimum pH of 10.9 and an optimum temperature of 35–40C. It was inhibited by KCN and alpha-tocopherol and was activated by NaF and NaN_3. The different optima temperature and pH indicated that the bacterial lipoxidase was different from soybean and cytochrome lipoxidases (Shimahara, *Kogyo Kagaku Zasshi 67* (8) 1164). Some lipoxidase activity was found in pig tissues, liver and muscle being the most active. In this case, the optimum pH was 5.0 to 6.4 and optimum temperature 25 to 30C (Wartenberg, *Zeszyty Nauk. Wyzszej Szkoly Rolniczej Wroclawiu, Weterynaria 16* (54) 57). A spectrophotometric method for the determination of lipoxidase activity was developed (Surrey, *U.S. At. Energy Comm. TID-* 18185, 25 pp.) (Surrey, *Plant Physiol. 39* (1) 65).

OXIDATION MECHANISMS

The mechanism of the autoxidation reaction was thoroughly investigated. The present knowledge and theories on this mechanism were reviewed (Garoglio, *Riv. Ital. Sostanze Grasse 41*, 181). Evidence was gathered indicating that actively autoxidizing fats contained two distinct peroxide forms. These forms, called I and II, had different decomposition rates in the presence of antioxidants. Peroxide I was the form more readily attacked by antioxidants. The distribution of the two peroxide forms in pure esters of fatty acids was the same as that in natural fats. Peroxide I was not detectable in fats after the induction period. It increased after active autoxidation started, and reached a maximum. Afterwards, further increase in peroxide value was due to an accumulation of Peroxide II. The formation and level of Peroxide I were not affected by the formation and level of Peroxide II. The level of Peroxide I was probably controlled by its own subsequent transformation rates (Kartha, *Indian J. Chem. 2* (3) 118).

Oleic acid was heated at 40C for 2,000 hr or at 80–100C for 180 hr, and the resulting products were characterized. The resulting organic phase was a mixture of C_6–C_9 saturated aldehydes. The aqueous phase was rich in formic acid. The major part of the uncondensable gases was CO_2 formed by oxidation of formic acid. The residue contained two hydrostearic acid isomers. The reaction was postulated to start with the formation of a peroxide aldehyde, which then decomposed to yield an immediately lower aldehyde or an enol form. This enol would then be peroxidized to an unstable aldehyde and formic acid (François and Loury, *Chim. Ind.* (Paris) *91* (6) 650).

The isolation from autoxidized methyl oleate of only hydroperoxide isomers at carbons 9 and 10 strongly supported the pi-electron complex theory of autoxidation (Kahn, *Oléagineaux 19*, 397).

Another monoethenoid, petroselinic acid, was heated at 120C with metal soaps as catalysts and the resulting products studied by GLC. The indications were that the high-temperature oxidation resulted in a rapid decomposition of peroxides, with the formation of dimeric products and resinous polymers. The peroxides decomposed then to ketols, which in turn oxidized to unstable dienones. These dienones aggregated in the presence of oxygen to form dimers, trimers, and higher polymers. The temperature had a much greater influence than the catalysts or the nature and length of the terminal chain (Skellon, *J. Oil Colour Chemists' Assoc. 46*. 1001).

The kinetics of the autoxidation of methyl linoleate emulsions in the presence of carbohydrates was interpreted to occur in the following fashion: RH = methyl linoleate; ROOH = methyl linoleate hydroperoxide). Initiation: $RH + O_2 \rightarrow ROOH$; ROOH + polyhydroxy compounds $\rightarrow$ ROO′ or R′. Propagation: $ROO' + RH \rightarrow ROOH + R'$; $R' + O_2 \rightarrow ROO'$. Chain termination: ROO′ + ROO, R′ + ROO′, and R′ + R′, all three give inactive products (Mabrouk, *JAOCS 41* (4) 331), see also (Quencer et al., *JAOCS 41* (10) 650) (Franks and Roberts, *J. Appl. Chem.* (London) *13*, 302) (Kritchevsky and Tepper, *Proc. Soc. Exptl. Biol. Med. 115*, 841). The examination of the vapors of autoxidizing methyl linoleate by GLC revealed the presence of saturated hydrocarbons, 90% of which was pentane (Horvat et al., *Nature 203* (4944) 523).

Methyl docosahexanoate was autoxidized at 35C under the air, and the polymerized products separated by partition chromatography. Three fractions were isolated which correspond to monomeric, dimeric, and trimeric compounds. All contained both –OOH groups and conjugated dienes. Polymerization caused a decrease in alpha-methylene groups and double bonds, almost the disappearance of *cis-trans* conjugated dienes and formation of rings containing oxygen (Fukuzumi and Miyakawa, *Kogyo Kagaku Zasshi 66*, 1320). In a similar experiment, the polymers formed upon oxidation of alkali-isomerized methyl docosahexanoate were isolated and studied (Fukuzumi and Ishida, *Ibid. 67*, 324). Other investigations characterized the changes resulting from the autoxidation of conjugated and

non-conjugated methyl docosahexanoates (Fukuzumi and Wakita, *Ibid. 66,* 1846). Finally, methyl docosahexanoate hydroperoxides were isolated and characterized (Fukuzumi et al., *Ibid. 66,* 1675).

ANTIOXIDANTS

The antioxidants and their importance in the preservation of dietary fats were discussed (Adamo, *Quaderni Merceol. 1* (1) 15) (Gerchuk, *Sb. Nauchn. Tr. Kooperat. Inst. po Vopr. Tovaroved i Organiz. Tekhn.,* (Moscow) *1963,* 3) (Paoletti et al., *Atti Acad. Med. Lombarda, Suppl. 17,* 700) (O'Neill, *Rept. Progr. Appl. Chem. 47,* 171). The group of phenolic antioxidants received considerable attention. The effect of various concentrations of four of them on the stability of lard was investigated. Maximum stability was attained with 1.5% cyclohexylphenol. All the phenolic antioxidants tested had lower activity than either tocopherol or gallates (Pokorný and Vašáková, *J. Inst. Chem. Tech.* (Prague) *5* (3) 11). In other experiments, catechol derivatives were demonstrated to be equal or better stabilizers than phenolic hydroquinol and pyrogallol derivatives (Pokorný et al., *Ibid. 5* (3) 173). The addition of Cu shortened the induction period in mixtures of phenolic antioxidants and fats (Janíček et al., *Z. Lebensm.-Untersuch.-Forsch 124,* (1) 17).

The synthesis and properties of BHA were described (Daniewski et al., *Tludszcze i Srodki Piorace 7* (6) 338). Dried fish were dipped in emulsions of BHA or BHT, surface active agents, and vegetable oil. BHA was more active than BHT in keeping fish from deterioration (Toyama and Saruya, *Nippon Suisan Gakkaishi 28,* 1020). The reverse was true in salted fish (Toyama and Saruya, *Ibid. 29,* 675). A BHT preparation containing also sorbitol, Span 20 and sucrose monostearate was superior to ordinary solid BHT preparations (*Ibid. 870*). Mixtures of BHA and Na erithorbate were effective in preventing the alteration of salted salmon (Ando et al., *Ibid. 28,* 823).

The preservation by BHA, BHT, and gallates was compared in several substrates. In suet, propyl gallate and BHT were better than BHA. In general, mixtures of antioxidants seemed to preserve better than an antioxidant alone (Tollenaar, *Proc. Pacific Sci. Cong., Pacific Sci. Assoc., 9th,* Bangkok, Thailand, 1957, *5,* 92 (Pub. 1963)). Mixtures of equal parts of propyl gallate and BHA and of propyl gallate and dibutylhydroxytoluene were effective in the preservation of ethyl oleate (Alemany-Verdaguer and del Pozo, *Galenica Acta* (Madrid) *16* (2) 109). Among several antioxidants tested, gallic acid esters were the best in preserving thermally treated fats (Waginaire, *Gattefosse- SFPA Bull. Tech. 1963* (60) 51) and goose fat (Rutkowski et al., *Zeszyty Nauk. Wyzszej Szkoly Rolniczej-Olsztynie 13* (3) 387). Color reversion of tallow could be best prevented by BHA, BHT or hydroquinone (Yamajako and Loury, *Rev. Franç. Corps Gras 10,* 513).

Several other antioxidants were investigated. Polyphosphates were tested in the preservation of frozen cod (Dyer et al., *J. Fisheries Res. Board Canada 21* (1) 101); wild rose hips in lard (Koeppe et al., *Med. Weterynar.* (Poland) *20* (3) 154); ascorbyl palmitate in cold stored butter (Koops, *Neth. Milk Dairy J. 18,* 38); tea leaf extracts or powder in cookies, mayonnaise, French dressing, and lard (Kihara and Inoue, *Kaseigaku Zasshi 15* (2) 67); sorbic acid and sorbates in margarine (Rutkowski and Holczak, *J. Inst. Chem. Tech.* (Prague) *5* (3) 129) (Stepanova et al., *Maslob. Zhir. Prom. 30* (3) 20). Phosphatides had protective action of the vitamin A in cottonseed oil used in cooking practices (Ismailov, *Tr. 2-oi (Vtoroi) Nauchn. Konf. po Vopr. Probl. Zhira v Pitanii, Leningrad 1962,* 366). Antioxidants were formed in lard during rendering at 110–120C (Rutkowski and Korzeniowski, *Roczniki Technol. Chem. Zywnosci 9,* 69). Tempeh powder was effective against oxidative deterioration (Ota et al., *Shokuryo Kenkyusho Kenkyu Hokoku 18,* 67). Other substances whose antioxidant properties were demonstrated were: flavone aglycones from vegetable extracts (György et al., *Nature 203* (4947) 870) and alkylated dihydroxynaphthalenes (Taeufel and Maune, *Fette Seifen Anstrichmittel, 66,* 260). The structure of two antioxidants isolated from oats was determined (Daniels and Martin, *Chem. Ind.* (London) *1964,* 2058).

Vitamin E at 0.05% was shown to retard rancidity in bottled olive oil (Fahmi and El Said, *Agr. Res. Rev.* (Cairo) *40* (3) 154). Mixtures (1:1) of olive oil and soybean oil were stored at 30C for 14 months with or without antioxidants. The oils containing antioxidants showed better keeping quality (Gutierrez, *Grasas y Aceites 15,* 249). The addition of soybean meal to waste and low quality fats improved their keeping quality (Pokorný et al., *J. Inst. Chem. Tech.* (Prague) 7 (1) 103). Alpha-tocopherol and ascorbic acid were ineffective in maintaining the oxidative stability of cereals (Anderson et al., *Food Technol. 17,* 1587).

Several substances usually grouped as antioxidants could act as pro-oxidants if the necessary conditions were provided. Propyl gallate, for example, enhanced the rate of initial oxidation of soybean or rapeseed oils if added to a concentration of 0.6% or higher (Pietrzyk, *Roczniki Technol. Chem. Zywnosci 9,* 29). Other so-called antioxidants showed similar effects (Pietrzyk, *Ibid. 9,* 81). Some pro-oxygenic properties were also detected in tocopherol (Dubois, *Ann. Technol. Agr. 13* (2) 97) (*Ibid.* 105). Carbonyl compounds of the type produced in browning degradation of sugars were also pro-oxidants (Anderson and Huntley, *JAOCS 41* (10) 686). Addition of dried algae reduced the stability of fats when they were stored in daylight (Pokorný et al., *J. Inst. Chem. Tech.* (Prague) *5* (3) 153).

Several chromatographic techniques were used for the qualitative and quantitative determination of a wide variety of antioxidants. Most numerous were quantitative thin-layer chromatography methods (Amano et al., *Shokuhin Eiseigaku Zasshi 5,* 333) (Rutkowski et al., *Roczniki Panstwowego Zakladu Hig. 14* (4) 361) (Sahasrabudhe, *J. Assoc. Off. Agric. Chem. 47* (5) 888) and qualitative (Ishikawa and Katsui, *Bitamin* (Japan) *30* (3) 203) (Jonas, *J. Pharm. Belg. 17* (3–4) 103) (Slonaker and Sievers, *Anal. Chem. 36,* 1130). GLC was also used (Choy et al., *J. Chromatog. 12,* 171) (Schweeke and Nelson, *J. Agr. Food Chem. 12* (1) 86) (Takahashi, *J. Assoc. Offic. Agr. Chemists 47* (2) 367), as well as paper chromatography (Sedlacek, *Fette Seifen Anstrichmittel 65,* 915) or chromatography on alumina followed by a fluorometric assay (Brueggemann and Zentz, *Z. Tierphysiol., Tierernaehr. Futtermittelk 18* (2) 99).

Non-chromatographic procedures were based on colorimetry (Nakamura et al., *Bunseki Kagaku 13* (1) 3) (Khomutov and Kulakovskaya, *Maslob.-Zhir. Prom. 30* (1) 12), fluorometry (Gordon et al., *J. Assoc. Offic. Agr. Chemists 47* (3) 516), measurement of methyl linoleate from oxidation (Quencer et al., *JAOCS 41* (10) 650) and titration with 2,4,6-tri-*tert*-butylphenoxy radicals (Paris et al., *Anal. Chem. 36* (7) 1332).

The Annual Review of Literature will be continued in November

New Shell Chemical Plant

Shell Chemical Co. recently broke ground for a $24.4 million plant at Geismar, La., in the New Orleans industrial complex.

C. W. Humphreys, company president, said that products of the plant, scheduled to go into operation in late 1966, will include: (1) ethylene oxide derivatives for further processing into plastics, textile chemicals, antifreeze and solvents, and (2) primary-range detergent alcohols, produced for manufacturers of household detergents and such industrial products as lubricating additives, cleaning compounds, emulsifiers and wetting agents.

The Geismar plant is the third in a new multi-million dollar complex the company is developing along the Gulf Coast. Other units in the complex are at Norco and Houston, Texas.