Most investigators seem to be of the opinion that the so-called copolymerization of styrene and drying oils proceeds by a chain reaction of the free radical type. Rinse (13) however has postulated that the reaction occurs via a proton shift because the usual catalysts for a free radical type of reaction have little or no effect on the course of the reaction whereas certain ketonic compounds such as anthraquinone, which are proton acceptors, promote the reaction.

It is not clear just how the peroxide functions in the reaction. Peterson postulated that a peroxide catalyst acts as a modifying agent, causing a reduction of the molecular weight of the polystyrene chains and thereby promoting greater compatability among the various molecular species. Our data lends support to this proposal.

The question whether the styrene actually copolymerizes with the oils and to what extent has not been conclusively answered. Although increasing the viscosity of the oils leads to more homogeneous products, this could be the result of greater mutual solubility as well as a result of copolymerization. Brunner and Tucker (2) have presented evidence based on ultraviolet and infrared absorption data that no interpolymerization between styrene and dehydrated castor oil occurs but that copolymerization between styrene and tung oil does occur. Petit and Fournier (11) have shown that no true interpolymerization between styrene and linseed oil takes place, but that a small amount of a condensation product consisting of one mole of styrene per mole of linolenic acid is formed.

Summary

Data and properties of products obtained by polymerizing styrene in the presence of drying and semi-drying oils have been presented. Evidence is given showing that conjugation in an oil or peroxide content are not of fundamental importance for obtaining homogeneous products. The increasing of the viscosity of the oils appears to lead to the formation of styrenated products of higher homogeneity.

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Reactions of Fatty Materials With Oxygen. IX.[1] Analytical Study of the Autoxidation of Methyl Oleate[2]

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AN investigation of the reliability of conventional analytical procedures for the quantitative determination of oxygen-containing functional groups likely to be encountered in autoxidation reactions was reported in an earlier paper (3), in which model compounds and mixtures of them were studied. In the absence of peroxide and oxirane groups, the analytical procedures were shown to be reliable. When peroxides were present, however, unusually high and non-reproducible values for carbonyl oxygen were obtained, and iodine and saponification numbers were often unreliable. Large proportions of oxirane compounds interfered with hydroxyl oxygen determination but peroxides did not interfere. The determination of acid number and peroxide and oxirane oxygen was reliable in the presence of all other functional groups investigated. Techniques were described for the accurate determination of functional groups when peroxide and oxirane groups were present. As a check on the reliability of the analytical methods finally employed,

good agreement was noted between total oxygen determined by difference from carbon and hydrogen analyses and total oxygen obtained from the sum of the analyses for the various oxygen-containing functional groups.

In the present paper we are reporting an analytical study of the autoxidation of methyl oleate irradiated with ultraviolet at 35°, 70°, and 100°C., employing the improved analytical techniques described earlier (3). The effluent gases were not studied in view of the systematic study of them by Hamilton and Olcott (1).

Experimental

Starting Material. The preparation of the methyl oleate employed has already been reported (3).

Oxidation Procedure. The oxidation procedures were the same as described previously (2) except that, in the oxidations at 35° and 100°, the quartz reaction flask was immersed in a constant temperature bath. In the oxidation at 70° heat from the ultraviolet lamps was sufficient to maintain the temperature to within ± 3°. Approximately 700 g. of methyl oleate were oxidized. The samples removed for analytical study were stored in the dark at 0° to −20° until analyzed. During the oxidation the

TABLE I

Autoxidation of Methyl Oleate at 35°; Millimoles of Oxygen Introduced
Per 100 Grams of Non-Volatile Autoxidized Substrate

Oxidation Time, Hrs.	Peroxide [a] Oxygen	Carbonyl Oxygen	Hydroxyl Oxygen	Oxirane Oxygen	Ester [b] Oxygen	Carboxyl [c] Oxygen	Total Oxygen Introduced	
							Sum of Individual Oxygen Analyses	Combustion [d]
0	0	0	0	0	0	0	0	0
6	2.0	0	0	0	1.5	0	3.5	—2.5
24	7.5	0	0	0	3.1	0	10.5	—4.6
48	13.7	0	0	0	4.0	0	17.6	10.3
72	23.7	0	0	0	6.3	0.7	30.7	21.8
98	29.3	7.2	0	0	5.6	0.2	42.3	30.9
123	40.0	12.8	0	0	8.7	0.4	61.9	31.8
152	42.5	17.2	0	0	8.4	1.0	69.1	47.1
200	51.8	12.8	0	7.5	6.4	4.0	82.5	78.1
299	66.8	7.2	6.8	8.7	9.2	6.1	104.8	99.6
408	69.3	30.9	12.8	11.2	20.5	9.8	154.5	134.3
504	87.5	31.2	20.6	10.0	21.3	13.6	184.2	166.8
600	103.7	48.4	20.0	16.8	18.0	18.5	225.4	169.3
700	96.2	57.2	21.8	17.5	19.3	22.8	234.8	178.7
800	110.6	64.3	30.0	18.1	22.1	27.6	272.7	236.8
1008	103.1	74.3	41.5	25.6	37.6	48.8	330.9	250.3
1200	100.0	76.5	39.0	27.5	39.0	62.7	344.7	295.0
1400	98.1	82.8	44.0	28.7	59.5	78.3	291.4	315.0
1656	84.3	95.9	34.0	33.1	61.7	97.3	406.3	386.2
1824	65.0	90.9	52.2	35.0	63.6	120.2	426.9	417.5
2000	69.3	92.2	39.7	40.6	71.0	135.1	447.9	450.9

[a] Calculated by dividing the percentage of active oxygen by 16 and multiplying by 1000. The value for pure methyl oleate hydroperoxide is 305 millimoles of peroxide oxygen per 100 g.
[b] Calculated from the difference between the ester number at various oxidation times and the ester number of the original methyl oleate.
[c] Calculated from the difference between the acid number at various oxidation times and the acid number of the original methyl oleate.
[d] Calculated from the difference between the total oxygen content at various oxidation times and the oxygen content of the original methyl oleate.

samples became pale-yellow and did not show any appreciable increase in viscosity. They remained homogeneous throughout the oxidations.

Analytical Methods. The methods and techniques have already been described (3).

Results and Discussion

Table I shows the distribution among the various functional groups of oxygen introduced (in millimoles of oxygen per 100 g. of non-volatile autoxidized substrate), in the autoxidation of methyl oleate at 35°. As a check on the reliability of the analytical methods, total oxygen introduced was also determined by difference from carbon and hydrogen analyses (last column of Table I). Figure 1 shows the rela-
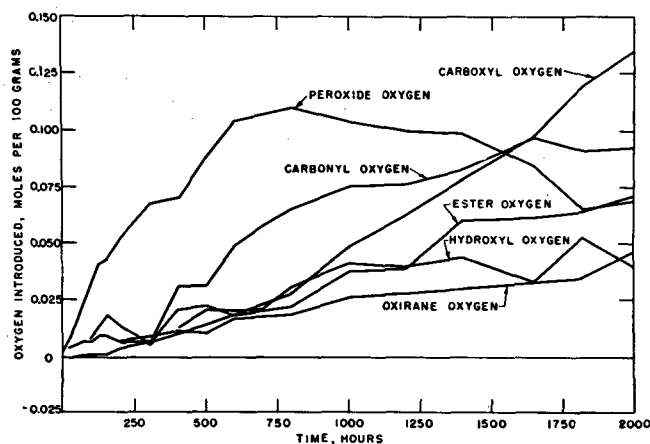

FIG. 1.

tionship among the various types of oxygen-containing functional groups present in methyl oleate autoxidized at 35°. Table II and Figure 2 summarize the data for methyl oleate autoxidized at 70°. Table III and Figure 3 summarize the data for methyl oleate autoxidized at 100°.

Peroxide oxygen was the first oxygen-containing group introduced which could be detected chemically at 35° and 70°. Peroxide oxygen rose fairly steadily

to a maximum of 110-120 millimoles per 100 g. of substrate in about 800 and 65 hours, respectively, before decreasing. At 100° the maximum in peroxide oxygen was only 87 millimoles per 100 g. in about 12 hours before decreasing at a rapid rate. In all cases the peroxide oxygen value levelled off, indicating an approximately equivalent formation and destruction. At 70° and 100° however the flattening of the peroxide oxygen curves was at much lower peroxide levels than at 35°.

At all temperatures, carbonyl oxygen rose less rapidly than did peroxide. At 35° carbonyl oxygen levelled off at about 90 millimoles per 100 g., after reaching a maximum of about 96 at about 1,656 hours. At 70° and 100° carbonyl oxygen rose to about 74 and 64 millimoles per 100 g. after about 144 and 24 hours, respectively, and then decreased slowly. Carbonyl oxygen was not detected for the first 98 hours at 35°, 6 hours at 70°, and 4 hours at 100°.

At 70° and 100° the hydroxyl oxygen curves were similar to the corresponding carbonyl oxygen curves both qualitatively and quantitatively. The maxima in hydroxyl oxygen were 69 and 76 millimoles per 100 g. of substrate at 144 and 96 hours, respectively. It was noted however that in the autoxidation at
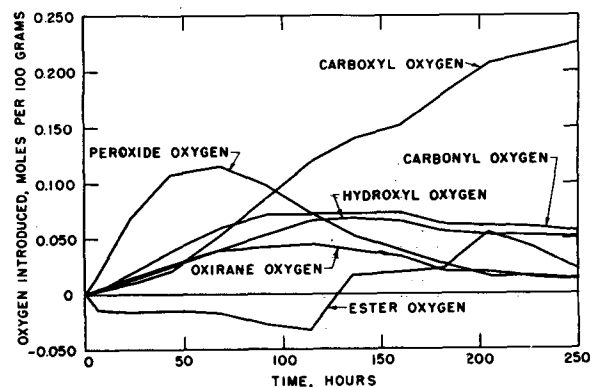

FIG. 2.

TABLE II

Autoxidation of Methyl Oleate at 70°; Millimoles of Oxygen Introduced
Per 100 Grams of Non-Volatile Autoxidized Substrate

Oxidation Time, Hrs.	Peroxide Oxygen	Carbonyl Oxygen	Hydroxyl Oxygen	Oxirane Oxygen	Ester Oxygen	Carboxyl Oxygen	Total Oxygen Introduced	
							Sum of Individual Oxygen Analyses	Combustion
0	0	0	0	0	0	0	0	0
6	16.1	3.8	5.0	5.6	—12.0	4.2	22.7	72.1
24	70.5	20.5	12.9	14.4	—16.0	9.8	112.1	123.1
48	107.8	43.1	26.9	26.0	—15.0	24.7	213.5	181.2
72	116.6	60.8	39.2	40.5	—17.0	53.6	293.7	260.0
96	98.1	71.1	54.0	43.7	—27.0	86.1	326.0	330.9
120	73.4	72.7	64.5	45.9	—32.0	117.8	342.3	355.0
144	53.4	73.9	68.9	40.2	17.0	140.8	394.2	388.7
168	48.9	72.4	65.0	33.9	20.0	151.7	391.9	411.2
192	26.0	63.2	55.6	20.6	24.0	181.5	370.9	447.5
216	16.3	62.1	53.2	19.8	54.0	207.1	412.5	461.8
240	16.0	59.1	51.9	15.6	41.0	216.6	400.2	469.6
264	12.3	56.5	49.8	12.2	20.0	225.9	376.7	471.2

100° the hydroxyl oxygen curve crossed that of carbonyl oxygen. At 35° the maximum in hydroxyl oxygen was only 44 millimoles per 100 g. of substrate (1,400 hours). This was surprising since it was anticipated that at the lower autoxidation temperature higher hydroxyl values would be obtained because hydroxyl groups would not be consumed in esterification reactions with carboxyl groups or in etherification reactions with oxirane groups. Hydroxyl oxygen (non-peroxidic) was not detected for the first 299 hours at 35°, 6 hours at 70°, and 4 hours at 100°.

After autoxidation for 2,000 hours at 35°, oxirane oxygen values were still increasing (41 millimoles per 100 g.). At 70° and 100° oxirane oxygen reached a maximum of about 46 and 44 millimoles per 100 g. in 120 and 24 hours, respectively, before decreasing slowly and levelling off at low values (about 10 millimoles per 100 g.). Oxirane oxygen was not detected for the first 200 hours at 35°, 6 hours at 70°, and 4 hours at 100°.

At all temperatures carboxyl oxygen climbed steadily without levelling off. At the end of the autoxidations the values for carboxyl oxygen were 135, 226, and 309 millimoles per 100 g. at 35°, 70°, and 100° after 2,000, 264, and 168 hours, respectively. Carboxyl oxygen was not detected for the first 72 hours at 35°, 6 hours at 70°, and 6 hours at 100°.

At 35° ester oxygen increased gradually throughout without levelling off after 2,000 hours (71 millimoles per 100 g.). At 70° ester oxygen reached a maximum of 54 millimoles per 100 g. in 216 hours and then decreased. At 100° ester oxygen was low

throughout the entire oxidation, the value hovering about 0. The negative values for ester oxygen in the autoxidations at 70° and 100° are probably a reflection of the more rapid increase in molecular weight of the autoxidized ester than in its ester oxygen content. Since ester oxygen introduced is calculated from the difference between the ester number at various oxidation times and the ester number of the original methyl oleate, increase in average molecular weight of the material being analyzed has a marked effect on the value obtained.

At 35° moderately satisfactory agreement was obtained throughout the autoxidation between total oxygen introduced determined from combustion analyses and total oxygen introduced determined from the sum of the individual analyses. At 70° and 100° however good agreement was noted only for the first 168 and 24 hours respectively, after which the combustion values for oxygen introduced were higher and the spread between the values became progressively larger. This difference in oxygen values can be accounted for by assuming the formation of ethers either by reaction of hydroxyl groups with oxirane groups, both of which decreased after reaching a maximum, or by the formation of oxygen-linked polymers (4). Both types of ether-forming reactions are favored by the higher temperatures. Neither type of ether oxygen would be detected analytically, but the formation of this type of oxygen linkage would be reflected in higher total oxygen values by combustion rather than from the sum of individual oxygen analyses. At all three temperatures about 2.5 to 3.0 atoms of oxygen were introduced per molecule of methyl oleate.

TABLE III

Autoxidation of Methyl Oleate at 100°; Millimoles of Oxygen Introduced
Per 100 Grams of Non-Volatile Autoxidized Substrate

| Oxidation Time, Hrs.	Peroxide Oxygen	Carbonyl Oxygen	Hydroxyl Oxygen	Oxirane Oxygen	Ester Oxygen	Carboxyl Oxygen	Total Oxygen Introduced	
							Sum of Individual Oxygen Analyses	Combustion
0	0	0	0	0	0	0	0	0
4	26.8	8.5	7.7	4.0	—4.1	0	40.4	30.3
6.5	54.2	17.8	10.6	9.8	—9.0	0.4	83.8	91.5
12	87.0	34.0	15.2	23.5	—32.8	16.7	143.6	140.3
24	58.9	64.3	32.4	44.0	—15.1	67.6	252.1	258.7
30.5	39.7	60.1	54.0	41.6	—28.4	81.7	248.7	282.8
48	21.7	61.2	61.8	31.9	—12.6	88.3	252.3	290.3
54.5	25.1	61.9	68.7	30.1	3.7	112.5	302.0	335.9
72	18.0	62.2	71.8	25.9	11.3	166.0	355.2	397.5
78.5	12.0	53.0	75.0	21.9	—6.7	182.5	337.7	415.0
96	6.5	50.6	75.6	13.3	—13.1	218.8	351.7	462.5
107	4.3	50.7	73.4	7.2	18.1	241.3	395.0	468.1
120	3.8	43.2	72.2	7.2	—1.4	260.9	385.9	490.9
144	1.9	41.4	62.5	7.1	—15.6	292.2	389.5	498.1
168	2.3	43.3	57.8	7.9	—22.0	308.9	398.2	489.3
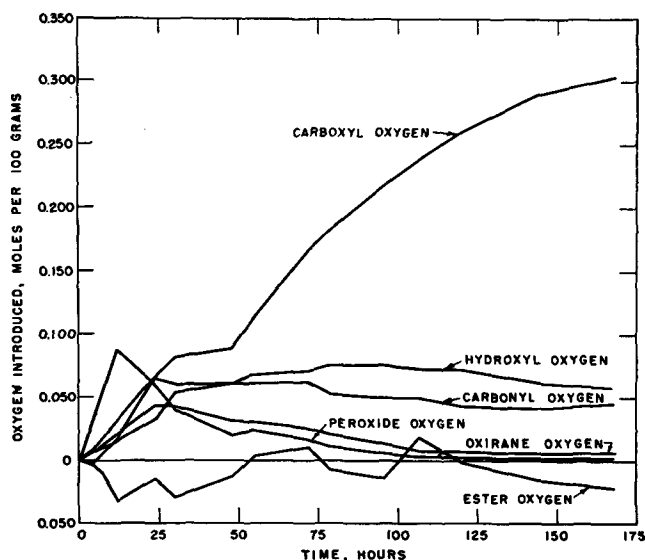
FIG. 3.

The iodine number (Wijs method) of the methyl oleate decreased smoothly with autoxidation time, more rapidly, of course, at the higher temperatures. When the oxidations were concluded, the iodine numbers of the methyl oleate autoxidized at 35°, 70°, and 100° were 22, 6, and 6, respectively. Attempts to correlate oxygen introduced with double bond disappearance gave no simple or understandable relationship.

The data presented and discussed indicate that the course of the autoxidation is exceedingly complex and that investigation of unfractionated oxidation mixtures is less likely to be productive of useful information for mechanism elucidation or the preparation of useful chemicals than fractionation followed by investigation of the behavior of pure intermediates. Fractionation work is now in progress and will be the subject of future reports. Furthermore, to direct

the oxidation reactions along preferred paths, highly selective oxidation conditions must be found.

Acknowledgment

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Summary

Methyl oleate, irradiated with ultraviolet, has been autoxidized at 35°, 70°, and 100°C. for 2,000, 264, and 168 hours, respectively. Samples were withdrawn at intervals and total oxygen introduced was determined by chemical analysis for peroxide, carbonyl, hydroxyl, oxirane, ester, and carboxyl oxygen.

Total oxygen introduced was also determined by difference from carbon and hydrogen analyses. In the autoxidation at 35° good agreement was obtained between the two methods for determining total oxygen introduced, over the entire time period studied. At 70° and 100° however good agreement was noted only during the early stages, after which the combustion values were higher and the spread between them became progressively larger. This difference is accounted for by formation of ethers, which could not be determined chemically. At all three temperatures about 2.5 to 3.0 atoms of oxygen were introduced per molecule of methyl oleate.

Even with such a comparatively simple substrate as methyl oleate the autoxidation reaction is exceedingly complex.

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Phase Relations Pertaining to the Solvent Winterization of Peanut Oil in Acetone-Hexane Mixtures[1]

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COMPLETE phase relation data on the solvent winterization of peanut oil in acetone (3) showed that commercial C.P. acetone did not show promise as a winterization solvent for peanut oil because of the formation of two liquid layers in the concentration and temperature ranges necessary for adequate winterization. It was found in the case of cottonseed oil (2) that separation into two liquid phases can be counteracted by the presence of a small proportion of a hydrocarbon, such as hexane, in the acetone.

The present report gives the phase relation data pertinent to the solvent winterization of a refined peanut oil in a solvent mixture consisting of 85 parts by weight of acetone and 15 parts of hexane. The

results show that with this solvent mixture a well-winterized peanut oil can be obtained without encountering two-liquid-layer formation.

Materials. A commercial refined and bleached peanut oil was used in the investigations. Its characteristics were: iodine value (Wijs), 94.1; free fatty acids as oleic, 0.34%; peroxide value, 4.2 millimoles per kg.; unsaponifiable matter, 0.35%; and moisture and volatiles, 0.04%.

Several hydrocarbon solvents were used with the commercial C.P. acetone in preparing the solvent mixtures. The commercial hexane and pentane used were Skellysolve B and F, respectively.[3] The isooctane was "99 mole % pure," and the cyclohexane was an Eastman Kodak Company product.[3]

[3] The mention of firms and trade products does not imply that they are endorsed or recommended by the Department of Agriculture over other firms or similar products not mentioned.