

Ion Exchange Resins and Ethyleneimine Polymer as Antioxidants II: Autoxidation Products

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ABSTRACT AND SUMMARY

The antioxidant effects of ion exchange resins and ethyleneimine polymer on the autoxidation products of methyl linoleate in a heterogeneous reaction system are discussed. Results from analyses of the various autoxidation products from linoleate samples with and without the antioxidants showed that the addition of the antioxidants did not change the original autoxidation mechanism of methyl linoleate. However, the antioxidants did retard the autoxidation in response to their antioxidant activity and, compared with a linoleate control, changed the yields of some autoxidized products such as an increased amount of conjugated diene hydroperoxides in linoleate samples with added ion exchange resins.

INTRODUCTION

The study of antioxidant effects on the autoxidation products of substrates is very important in elucidating the autoxidation reaction mechanism. In a previous report (1), henceforth referred to as "the companion paper," ion exchange resins (IER) and ethyleneimine polymer (EP) were evaluated in a heterogeneous system for their antioxidant characteristics and for their effects upon the termination reaction in the autoxidation of methyl linoleate. In this report IER and EP are evaluated for their specific roles in the reaction mechanism and for their effects upon the quantitative change of autoxidation products derived from oxidized methyl linoleate (ML). Also reported are the different effects between homogeneous and heterogeneous reaction systems of the antioxidants upon the autoxidation products.

EXPERIMENTAL PROCEDURE

Materials

Methyl linoleate was used as the autoxidation substrate, and IER and EP as antioxidants. Properties of these materials are shown in the experimental section of the companion paper (1).

Autoxidation Procedure

This procedure followed that outlined in the experimental section of the companion paper, but the ML samples to be oxidized were prepared to contain 2.00% by wt of antioxidants. Weight gains with the autoxidation of samples were determined by the weighing procedure. The induction period was defined as the time (hr) required to gain the oxidation weight gain of 10 mg just before quick elevation in weight gains.

Analytical Procedure

Infrared, ultraviolet (UV), and electron spin resonance (ESR) spectra, peroxide values (PV), molecular weights (MW), and refractive indices were determined on ML samples, with and without IER and EP, from various autoxidation levels in order to examine the effects of antioxidants on the autoxidation of ML. Infrared spectra were obtained with a Shimadzu IR-27B instrument and a grating IR spectrophotometer (Japan Spectroscopic Co., Tokyo,

Japan, model DS-402G). Samples were diluted with carbon tetrachloride and run in 0.10 and 9.97 mm NaCl cells. The 9.97 mm cell was used to determine PV (2) due to the hydroperoxy group absorbing at 3520 cm^{-1} and the amount of hydroxyl group at 3600 cm^{-1} in autoxidized samples which were diluted to 3.98 g/l for the IR analyses. The 0.10 mm cell was used to determine the amounts of: (a) conjugated *cis,trans*- (at 948 cm^{-1}) and *trans,trans*-dienes (at 988 cm^{-1}) (3); (b) isolated *trans* double bond at 968 cm^{-1} (4); and (c) the absorptivity due to the alpha and active methylene groups absorbing at 3020 cm^{-1} (5), in autoxidized samples at 66.67 g/l concentration range. The stretching vibrational band due to hydroperoxy groups appeared at 3450 cm^{-1} when observed by 0.10 mm cell, and appeared at 3520 cm^{-1} when observed by 9.97 mm cell. The 3520 cm^{-1} band was due to nonassociated hydroperoxy groups, and that at 3450 cm^{-1} associated hydroperoxy groups. Peroxide values were calculated from the 3520 cm^{-1} band in IR spectra determined with 9.97 mm cell at the low concentration (3.98 g/l) of autoxidized samples, where hydroperoxides in the samples did not form intermolecular hydrogen bonds. Peroxide values (meq/kg) were measured by iodometry (6). Ultraviolet spectra were determined with a Shimadzu UV-200 instrument. The amounts of conjugated diene (7) and $\alpha,\beta,\gamma,\delta$ -unsaturated carbonyl were calculated from UV spectra. The detection and the quantitation of free radicals produced in the autoxidation of ML samples were carried out at 20°C using an ESR spectrometer (Japan Electron Optics Lab. Co., Tokyo, Japan, model JES-1X). Molecular weights were determined with a Hitachi Perkin-Elmer 115 type apparatus (by evaluating the vapor tension of sample solutions in benzene). Refractive indices were measured at 20°C with an Abbe refractometer.

RESULTS AND DISCUSSION

Infrared spectra observed with 0.10 mm NaCl cell for autoxidized samples with and without antioxidants showed increases (I) or decreases (D) in the following absorption bands: hydroxyl (I) at 3600 cm^{-1} , hydroperoxy (I) at 3450 cm^{-1} , alpha methylene (D) at 3020 cm^{-1} , aldehyde (I) at 1725 cm^{-1} , ketone (I) at 1715 cm^{-1} , active methylene (D) at 1400 cm^{-1} (the increase of the absorption band between $1400\text{--}1100\text{ cm}^{-1}$ was due to the formation of polymeric products), cyclic peroxides (I) at 1100 cm^{-1} , conjugated *trans,trans* diene (I) at 988 cm^{-1} , conjugated *cis,trans* diene (I) at 982 and 948 cm^{-1} , conjugated diene (I) at 1650 and 1600 cm^{-1} , isolated *trans* double bond (I) at 968 cm^{-1} , and isolated *cis* double bond (D) at 913 cm^{-1} . Formation of hydroxyl and aldehyde functional groups was negligible even in highly autoxidized samples. Information obtained from the IR spectra suggests the same ML autoxidation mechanism occurs with or without antioxidants. The diminution of the alpha methylene groups (3020 cm^{-1}) with increasing autoxidation time is shown in Figure 1A. The decrease in the alpha methylene content of oxidized samples was confirmed by noting a corresponding decrease in the active methylene proton signal at 2.80 ppm in nuclear magnetic resonance (NMR) spectra. Therefore, IR data seems to show the disappearance of the active methylene group which is one of alpha methylene groups in

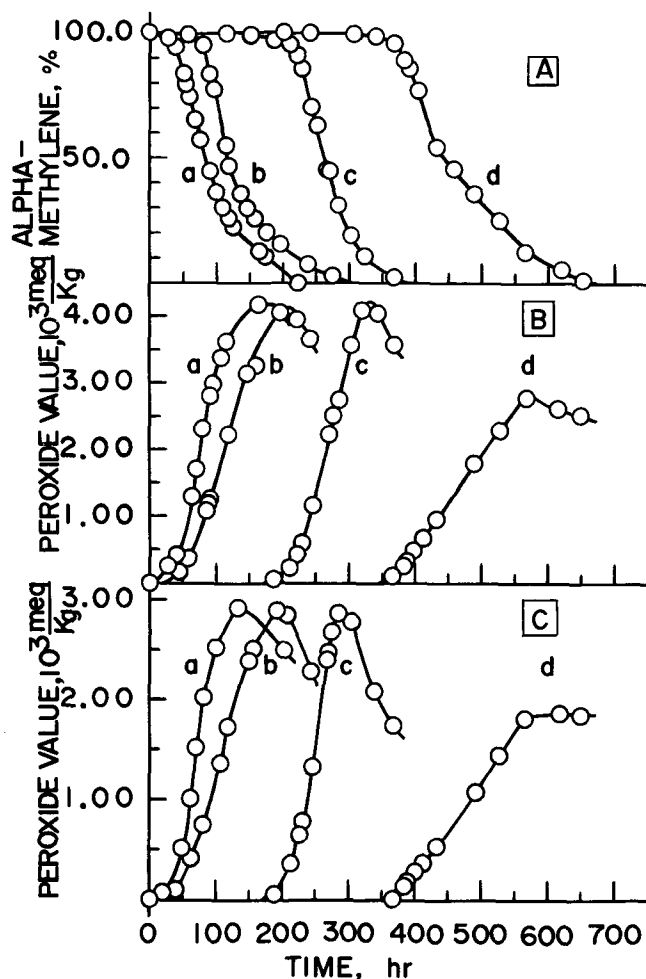


FIG. 1. Effects of ion exchange resins and ethyleneimine polymer upon the diminution of the alpha methylene groups (A), and upon the hydroperoxide formation, obtained from iodometry (B), and from IR spectra (C), in the autoxidation of methyl linoleate. (a) Control, (b,c) Amberlite IR 45 treated and untreated with H_2O_2 , and (d) ethyleneimine polymer, autoxidation temperature— 36.5 ± 0.5 C; oil thickness—1.03 mm; antioxidant concentration—2.00% by wt (a, b, c, and d are the same antioxidants in later figures unless otherwise specified).

ML samples. The addition of IR 45 or EP noticeably retarded the time, compared to the control, when the alpha methylene content began to decrease, but the decrease in the alpha methylene content of the IR 45 or EP samples approaches that of the control if the alpha methylene concentration is plotted against oxidized ML weight gain in stead of time. These results show that autoxidation of ML samples with and without the antioxidants have the same loss in the alpha methylene content during autoxidation for the same ML weight gain. The effects of IR 45 and EP on the PV formation in oxidized ML are shown in Figure 1B and 1C. As can be noted in the figure, the rate of PV formation and the maximum PV of the control (a) and samples with IR 45 (b and c) are approximately the same, but samples with added EP had a slower rate of hydroperoxide formation as well as a lower PV maximum. These results are shown in Figure 2 where correlations can be noted between weight gains and PV from oxidized samples with and without added antioxidants. When calculating the theoretical curve data, it was assumed that the oxygen absorbed during autoxidation (weight gains) was quantitatively related to hydroperoxide formations. The correlation between weight gains and PV for the samples with and without IER agreed with the theoretical curve until the autoxidized ML has a weight gain of 85 mg or a

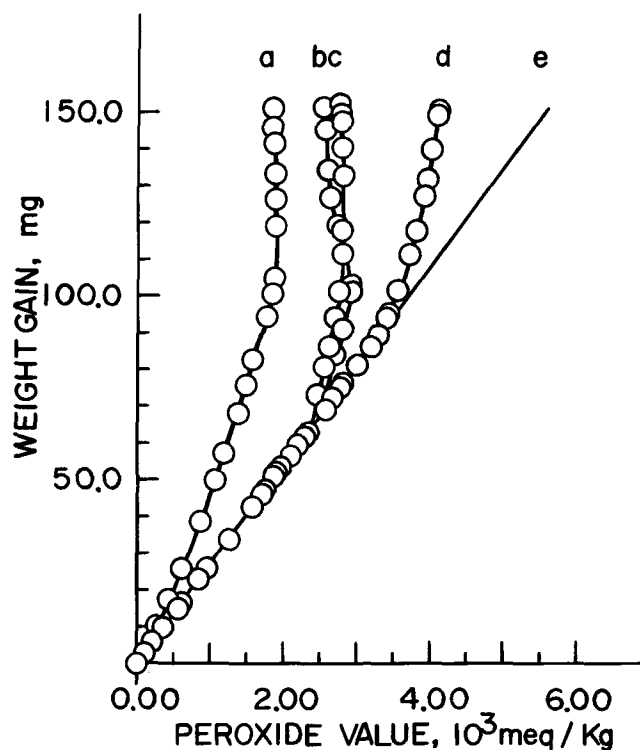


FIG. 2. Relations between peroxide value and weight gain in the autoxidation of methyl linoleate. (a) Peroxide value (PV) obtained from IR spectra of the autoxidized samples with added ethyleneimine polymer, (b) PV obtained by the iodometry for the autoxidized samples with added ethyleneimine polymer, (c) PV obtained from IR spectra of the autoxidized samples with and without ion exchange resins, (d) PV obtained by iodometry for the autoxidized samples with and without ion exchange resins, and (e) theoretical correlation.

PV of 3.2×10^3 meq/kg as determined from iodometry measurements, and 63 mg or 2.3×10^3 meq/kg as determined from IR spectra. But, from ML samples with added EP, the above corresponding values are 64 mg or 2.35×10^3 meq/kg in the correlations from iodometry data and 10 mg or 0.47×10^3 meq/kg in the correlations from IR data. The ML samples with added EP and PV-weight gain correlations which noticeably differed from the theoretical line. The deviations might result from the coupling of the imino radicals from EP with peroxy radicals from oxidized ML as shown in Figure 6 of the companion paper. The PV calculated from IR spectra shows the hydroperoxide content able to exist in the nonassociated condition. As shown in Figure 2 curve c in the samples with and without IER, the 3520 cm^{-1} band increased quantitatively until the autoxidized ML had a weight gain of at least 63 mg or a PV of at least 2.3×10^3 meq/kg. But, when ML had an oxidation wt gain of over 63 mg, the 3450 cm^{-1} band in addition to the 3520 cm^{-1} band appeared and increased with the autoxidation time, even by sufficient dilution (1.00 g/l) of IR samples. Therefore, the 3450 cm^{-1} band seemed to be due to the hydroperoxides forming intramolecular hydrogen bonds. The PV due to the hydroperoxides forming intramolecular hydrogen bonds might correspond to the difference between the PV determined by iodometry and that calculated from IR spectra at the 3520 cm^{-1} band. On the other hand, as shown in Figure 2 curve a in added EP samples, the 3520 cm^{-1} band increased quantitatively until the autoxidized ML had a weight gain of at least 10 mg or a PV of at least 0.47×10^3 meq/kg. But, when ML had an oxidation weight gain of over 10 mg, the 3450 cm^{-1} band appeared. As shown in Figure 2, curve d in the ML samples with and without IR 45, the amount of oxygen absorbed in the samples was quantitatively used to form hydroper-

TABLE I
Comparison of Peroxide Value ($\times 10^3$ meq/kg), Measured by Iodometry, are Influenced by Resin Type

| Samples | Weight gain, mg | | | | | | | |
|--|-----------------|------|------|------|------|-------|-------|-------|
| | 5.0 | 10.0 | 25.0 | 50.0 | 75.0 | 100.0 | 125.0 | 150.0 |
| Dowex 50W | 0.21 | 0.48 | 1.23 | 2.14 | 2.76 | 3.34 | 3.77 | 3.92 |
| IRC 50 | 0.26 | 0.48 | 1.26 | 2.17 | 2.85 | 3.38 | 3.77 | 3.78 |
| IRA 400 (Cl) | 0.24 | 0.48 | 1.20 | 2.15 | 2.98 | 3.62 | 4.00 | 4.30 |
| IRA 400 (OH) | 0.22 | 0.45 | 1.21 | 2.09 | 2.95 | 3.51 | 3.85 | 4.18 |
| IRA 410 (Cl) | 0.26 | 0.40 | 1.21 | 2.14 | 2.89 | 3.38 | 3.69 | 3.93 |
| IRA 410 (OH) | 0.24 | 0.40 | 1.26 | 2.13 | 2.86 | 3.37 | 3.78 | 4.05 |
| IRA 93 | 0.25 | 0.45 | 1.06 | 2.02 | 2.76 | 3.40 | 3.79 | 3.93 |
| IR 45 | 0.27 | 0.50 | 1.24 | 2.15 | 2.81 | 3.20 | 3.56 | 3.76 |
| IR 45 treated with H ₂ O ₂ | 0.22 | 0.44 | 1.27 | 2.13 | 2.80 | 3.25 | 3.63 | 3.73 |
| Ethyleneimine polymer | 0.25 | 0.47 | 1.09 | 1.75 | 2.32 | 2.77 | 2.64 | 2.46 |
| Control | 0.25 | 0.49 | 1.20 | 2.30 | 3.00 | 3.45 | 3.83 | 4.13 |

oxides until the samples were autoxidized to weight gains of 85 mg or a PV of 3.2×10^3 meq/kg. Therefore, the chain propagation due to equations, $ROOH \xrightarrow{RO\cdot} RO\cdot + \cdot OH$ then $RO\cdot + RH \rightarrow ROH + \cdot R$, would be negligible until the samples were autoxidized to weight gains of 85 mg or a PV of 3.2×10^3 meq/kg. On the other hand, in Figure 2 curve b it is shown that in samples with added EP the amount of oxygen absorbed in the samples was quantitatively used in hydroperoxide formations until the samples were autoxidized to weight gains of 64 mg or a PV of 2.35×10^3 meq/kg. The PV at specific weight gains of oxidized samples, with and without antioxidants, is shown in Table I. The data in Table I show that oxidized ML samples either as a control or with added IER have approximately the same PV when all the samples had been oxidized to a given weight gain, however, ML with added EP had PVs lower than the control when the oxidation level was 50 mg or greater. Therefore, from the initial autoxidation time to the 50 mg oxidation level the coupling of EP imino radicals with peroxy radicals might be too small to produce a noticeable difference in the hydroperoxide contents of the control and samples with added EP. This phenomenon may be due to the high stability of imino radicals in the heterogeneous reaction systems as shown in Figure 6 of the companion paper.

Conjugated diene contents calculated from UV spectra of ML samples with and without antioxidants are shown in Figure 3A, and the conjugated diene contents of samples for given weight gains are shown in Table II. It may be of interest that samples with added IER had larger conjugated diene contents compared to both the control and the EP samples. On the other hand, samples with added EP has similar conjugated diene contents as the control, though EP samples had diene formation rates less than that of the control. As can be noted in the table, the formation of conjugated dienes during the autoxidation of ML was independent of the acidity or basicity of IER, and of the sort of IER. The antioxidant properties of IER do not appear to be requisite for conjugated diene formations. When standing ML samples with added IER, at 36.5 ± 0.5 C, under the 10^{-3} mm Hg pressure, ML samples were not isomerized to the conjugated diene isomers. Therefore, large conjugated diene formation might result from the autoxidation of ML samples with added IER. The large conjugated diene values of the added IER samples were probably due to the specific absorption character of IER antioxidants. As noted in the Table I of the companion paper, the small antioxidant activities of IER, excluding IR 45, might also result from the stabilization of alkyl or peroxy radicals produced in the autoxidation of ML due to the affinity, such as a hydrogen bond, with IER antioxidants. This is based on the fact that autoxidation of samples containing IER, except for those with IR 45, did not chemically alter the added antioxidants.

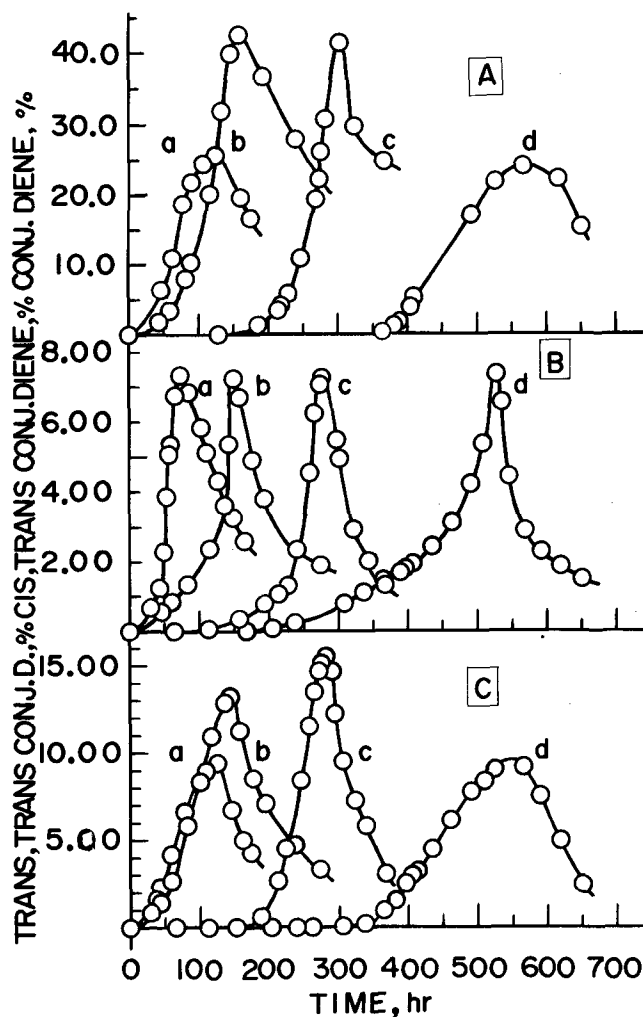


FIG. 3. Effects of ion exchange resins and ethyleneimine polymer upon the conjugated diene formation calculated from UV spectra (A), and upon the conjugated cis,trans (B), and trans,trans (C) diene formation, calculated from IR spectra in the autoxidation of methyl linoleate.

The conjugated cis,trans and trans,trans diene contents calculated from IR spectra for the samples with and without antioxidants are shown in Figure 3B and 3C. The figure shows that conjugated cis,trans dienes are formed first to have their maximum values in autoxidation of ML samples with and without added IER or EP, then with increasing time they convert to conjugated trans,trans diene configurations. This phenomenon of cis,trans ceding to the trans,trans configuration is confirmed from UV evidence in that the absorption maximum for conjugated dienes contained

TABLE II

Comparison of Conjugated Diene Content (%), Calculated from UV Spectra, and Influenced by Resin Type

| Samples | Weight gain, mg | | | | | | | |
|--|-----------------|------|------|------|------|-------|-------|-------|
| | 5.0 | 10.0 | 25.0 | 50.0 | 75.0 | 100.0 | 125.0 | 150.0 |
| Dowex 50W | 3.3 | 5.8 | 14.8 | 21.1 | 29.4 | 34.6 | 35.1 | 29.6 |
| IRC 50 | 3.0 | 6.0 | 14.8 | 21.5 | 31.4 | 39.4 | 42.0 | 30.7 |
| IRA 400 (Cl) | 3.3 | 6.0 | 15.2 | 21.5 | 27.8 | 30.7 | 31.6 | 28.6 |
| IRA 400 (OH) | 3.4 | 6.4 | 15.6 | 21.5 | 28.7 | 35.1 | 36.2 | 26.4 |
| IRA 410 (Cl) | 3.0 | 5.7 | 15.2 | 23.5 | 33.2 | 39.3 | 38.6 | 27.6 |
| IRA 410 (OH) | 3.3 | 6.2 | 15.0 | 21.1 | 30.4 | 40.2 | 48.5 | 31.0 |
| IRA 93 | 3.3 | 6.1 | 15.3 | 23.7 | 35.6 | 45.4 | 51.9 | 36.2 |
| IR 45 | 3.1 | 5.9 | 15.5 | 21.9 | 32.8 | 41.0 | 29.5 | 24.3 |
| IR 45 treated with H ₂ O ₂ | 3.0 | 6.0 | 15.2 | 20.0 | 35.6 | 42.7 | 39.0 | 30.5 |
| Ethyleneimine polymer | 2.9 | 5.9 | 9.3 | 17.0 | 22.0 | 24.0 | 22.8 | 12.3 |
| Control | 3.1 | 6.2 | 8.6 | 15.1 | 20.2 | 23.8 | 24.8 | 22.1 |

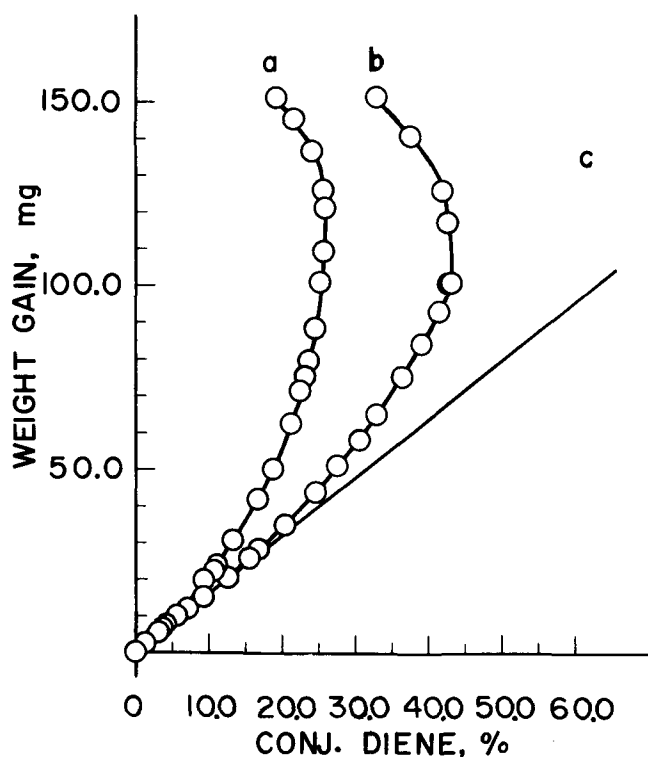


FIG. 4. Relations between conjugated diene content and weight gain in the autoxidation of methyl linoleate. (a) Control and ethyleneimine polymer, (b) ion exchange resins, and (c) theoretical correlation.

in the autoxidized samples shifted from 233 to 231 nm with increasing autoxidation time. Results from IR spectra obviously show that the additions of IER or EP do not change conjugated *cis,trans* diene contents relative to the control, but large differences are noted for conjugated *trans,trans* diene contents of the IER samples in comparison with the control. The noticeable amounts of conjugated *trans,trans* dienes in the IER samples might be due to their relative low steric hindrances for the affinity with the IER antioxidants.

Correlations between conjugated diene contents calculated from UV spectra and weight gains with the autoxidation of samples with and without antioxidants are shown in Figure 4. When calculating the theoretical curve data, it was assumed that the oxygen absorbed during the autoxidation (weight gains) was quantitatively related to conjugated diene formations. The formation of conjugated dienes followed the theoretical curve until oxidized ML had a weight gain of at least 13 mg for ML with added EP or at least a weight gain of 30 mg for ML with added IER. Since the

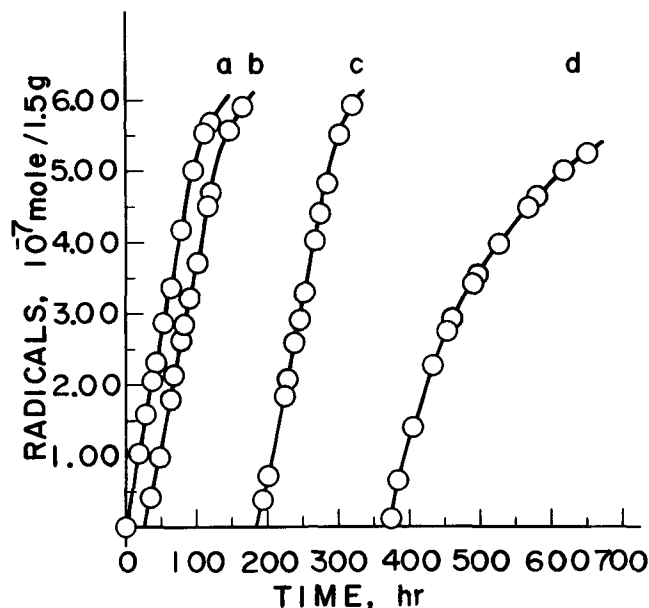


FIG. 5. Effects of ion exchange resins and ethyleneimine polymer on the free radical formation due to the autoxidation of methyl linoleate (measured with an electron spin resonance spectrometer).

observed PV followed the theoretical curve (PV versus weight gain), as shown in Figure 2, to a higher autoxidation level (weight gain) than did the above conjugated dienes to their theoretical curve, the conjugated dienes observed in the autoxidized samples might come from the conjugated diene hydroperoxides. Therefore, the autoxidation of ML samples with added IER resulted in considerable amounts of conjugated *trans,trans* diene hydroperoxides (see section C in Fig. 3). The large amounts of conjugated *trans,trans* diene in the IER samples have not been noted in normal homogeneous reaction systems containing antioxidants.

The change of the free radical (g -value = 2.00611) concentration in ML samples with respect to oxidation time is shown in Figure 5. The free radical species might be the peroxy radicals due to $R \cdot + O_2 \rightarrow ROO \cdot$ until the samples were autoxidized to a weight gain of 85 mg or a PV of 3.2×10^3 meq/kg for the samples with and without IER, and a weight gain of 64 mg or a PV of 2.4×10^3 meq/kg in samples with added EP. That they are peroxy radicals is based upon data in Figure 2 (the agreement of the correlation between weight gains and PV with the theoretical curve). Figure 5 appears to show that the free radical formations increase linearly from the initial autoxidation stage after the induction periods, then deviate from its linearity near the maximum radical concentration values. The decrease in the free radical formation near the maximum

values probably results from polymerization due to the coupling of free radicals. In comparison to the control, the addition of IER to ML did not effect the rate of formation nor the final free radical concentration, but merely retarded the time when they would begin to form, as given in Figure 5 lines a versus b and c. In contrast to ML with IER, the ML with added EP lowered the rate of the free radical formation and the final radical concentration, as shown in lines b and c versus d in Figure 5. The rate of the free radical formation in Figure 5 was 5.70×10^{-9} mole/hr for the samples with and without IER, and 4.62×10^{-9} mole/hr for the samples with EP. The value for samples with and without IER is indicative of new peroxy radicals formed due to the initiation reaction, $RH + O_2 \rightarrow R\cdot + \cdot OOH$ then $R\cdot + O_2 \rightarrow ROO\cdot$, at least during the autoxidation process when the effects of equations, $ROOH \rightarrow RO\cdot + \cdot OH$ and $RO\cdot + RH \rightarrow ROH + \cdot R$, are negligible. The low slope and low radical concentration value in the ML samples with added EP might be the result of imino radicals (due to EP in the chain termination reaction) reacting with a part of the ML derived free radicals after the EP oxidation induction period. This supposition is supported by the slow disappearance of the imino radicals in the EP samples after its induction period. On the other hand, no observable changes in PV and weight gains during the initial autoxidation stage of the induction periods and slight increases in PV and weight gains near the end of the induction periods obviously shows: the autoxidation of ML is suppressed by the addition of the IER and EP antioxidants; oxidation of ML gradually increased the propagation rate of the free radical chain (due to $ROO\cdot + RH \rightarrow ROOH + R\cdot$) with a decrease of antioxidants, and reached a maximum chain propagation rate after the antioxidants disappeared. The slope of the weight gains or PV for the autoxidized samples after the induction periods was 3.98×10^{-5} mole/hr for the samples with and without IER, and 1.78×10^{-5} mole/hr for the sample with EP. The 3.98×10^{-5} mole/hr value for samples with and without IER indicates the overall dynamics of $RH + O_2 \rightarrow R\cdot + \cdot OOH$, $R\cdot + O_2 \rightarrow ROO\cdot$ and $ROO\cdot + RH \rightarrow ROOH + \cdot R$ may be the longest chain propagation reaction under the experimental conditions of this study. Also, because the rate of free radical formation plus the rate of weight gain and PV of the IER samples were similar to those of the controls, the IER antioxidant probably did not effect the oxidation of ML after the IER induced induction period. Other significant observations on the oxidation of ML include data on isolated trans double bond calculated from IR spectra, the average MW of oxidized ML, the $\alpha,\beta,\gamma,\delta$ -unsaturated carbonyl content (absorption maximum = 272 nm) calculated from UV spectra, and refractive index at 20 C; the data are shown in Figure 6A, 6B, 6C, and 6D, respectively. These additional results show polymerized and unsaturated carbonyl products derived from autoxidized ML gradually increased when ML had an oxidation weight gain of over 70 mg for the samples with and without IER, and of over 50 mg for added EP samples. Even then, compared to the control, addition of IER to ML, with the exception of IR 45, resulted in similar yields of various autoxidation products, except for the conjugated diene contents. All of the analytical results show that the addition of the IER and EP antioxidants to ML which formed a heterogeneous reaction system did not change the original autoxidation mechanism

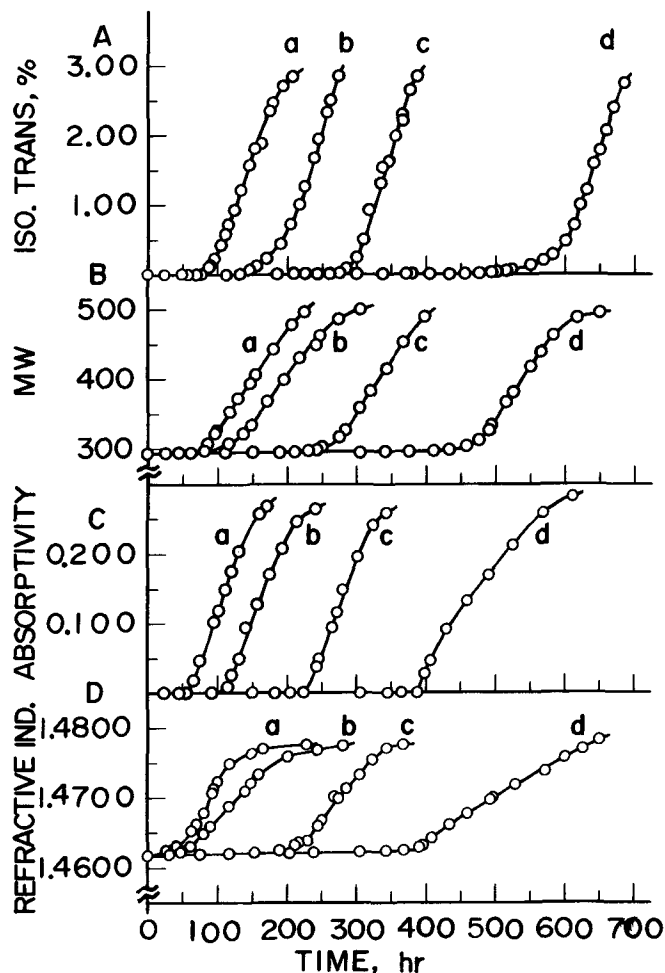


FIG. 6. Effects of ion exchange resins and ethyleneimine polymer upon isolated trans double bond (A), average molecular weight (B), $\alpha,\beta,\gamma,\delta$ -unsaturated carbonyl (C), and refractive index (D) at 20 C in the autoxidation of methyl linoleate.

of ML. However, the antioxidants did retard the autoxidations according to their individual antioxidant activities, and did affect the yields of some autoxidized products, such as increased the amount of conjugated trans,trans diene hydroperoxides in ML with added IER and decreased the rate of PV formation in ML with added EP.

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