Ion Exchange Resins and Ethyleneimine Polymer as Antioxidants: I. Activity and Mechanism

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ABSTRACT

The antioxidant activity of ion exchange resins and ethyleneimine polymer was determined in methyl linoleate free from natural antioxidants and metals. Superior antioxidant activities were recognized in an ion exchange resin with NH groups and in the ethyleneimine polymer. The antioxidant activities in these heterogeneous reaction systems increased in linear proportion to the amount present. These antioxidant activities in the heterogeneous reaction system were mainly owing to their ability to donate hydrogen to the peroxy radicals produced in the autoxidation of methyl linoleate. The antioxidant radicals produced in these cases were very stable and generally couldn't participate in the increase of the induction periods in the autoxidation of methyl linoleate by terminating the peroxy radicals. These results have never been obtained in the homogeneous reaction system but are characteristic in the heterogeneous one.

INTRODUCTION

The antioxidant activity of various phenols and amines has been investigated by many workers. But the use of these antioxidants as food additives has been subjected to various limitations by reason of being taken in vivo systems, because most of these antioxidants were effective in the homogeneous reaction system. Therefore, many studies on natural antioxidants, such as tocopherols which are nontoxic, have been performed actively in recent years. However, it is regrettable that natural antioxidants having the superior antioxidant activity have never been found. This problem on the toxicity of antioxidants might be easily solved by the use of antioxidants forming heterogeneous reaction systems. The antioxidant activity is generally dependent on its power of eliminating the peroxy radicals from the free radical chain process in the autoxidation of substrates. From this viewpoint, the necessary condition for antioxidants in heterogeneous reaction systems might be that the antioxidants can donate hydrogen atoms to peroxy radicals and turn into antioxidant radicals that do not dissolve into the autoxidized substrates, or that the antioxidants originally containing the radical species easily couple with peroxy radicals. In the former reaction, hydroperoxides would be produced in the presence of the antioxidants, but in the latter reaction hydroperoxide formation itself would be prevented. In this paper, the antioxidant activity and its mechanism are discussed for the heterogeneous systems of ethyleneimine polymer (EP) and ion exchange resins (IER), both having the superior antioxidant activity of the NH amine group. Also discussed are the different antioxidant effects shown by homogeneous and heterogeneous reaction systems.

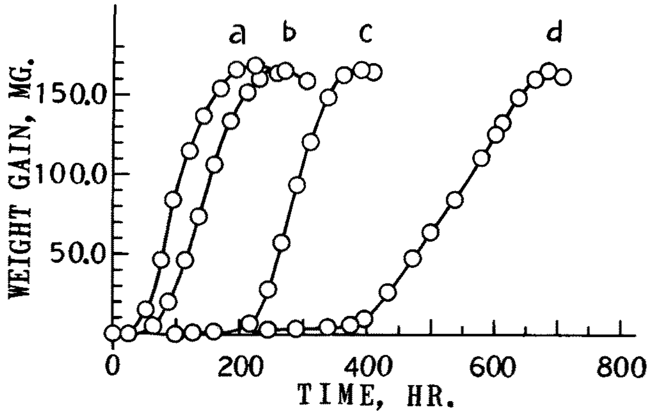

FIG. 1. Effects of ion exchange resins and ethyleneimine polymer (2.00% by wt) on weight gain in the autoxidation of methyl linoleate. (a) Control. (b,c) Amberlite IR 45 treated and untreated with H_2O_2. (d) Ethyleneimine polymer, autoxidation temperature 36.5 ± 0.5 C, oil thickness 1.03 mm.

EXPERIMENTAL PROCEDURE

Materials

The autoxidation substrate, methyl linoleate (ML, 99.9% purity as determined by GLC), was prepared from safflower fatty acids followed by the urea adduct formation, methyl esterification (1), and column chromatography with silicic acid to remove a trace of peroxides and pigments. Removal of natural antioxidants and metals from ML was confirmed by the ferric chloride:2,2′-bipyridine method (2) and by atomic absorption spectra, respectively. IER as antioxidants, such as IR 45, IRC 50W, IRA 93, IR 120B, IRA 400, and IRA 410, provided by Organo Co. (Tokyo, Japan), and Dowex 50Wx8 (100-200 mesh), provided by Muromachi Chem. Ind. Co. (Tokyo, Japan), were commercial products and rigid and spherical substances. The standard crosslinking degree of these IER was 8 in the divinyl benzene percent unit. These IER were oxidized at room temperature for 15 hr in the presence of H_2O_2, ethylenediamine tetraacetic acid, and sodium tungstate in ethyl alcohol (3), and used as antioxidants. EP as an antioxidant was a commercial product (Tokyo Casei Ind. Co., Tokyo, Japan; Extra Pure Grade). All antioxidants were used in the anhydrous condition after drying for 1 week under 10^{-3} mmHg pressure over P_2O_5.

Autoxidation Procedure

ML (1.5000-1.5005 g) and antioxidants (1.00-30.00% by wt of ML) were added to beakers (4.1 cm diameter), respectively. The autoxidation of ML and the samples containing IER or EP was carried out at 36.5 ± 0.5 C in an incubator under air atmosphere, after the volatile materials contained in the samples were removed for 1 hr at 30 ± 1 C under 10^{-3} mmHg pressure as described in the previous literature (1). Then the oil thickness in the beakers was 1.03 mm. The weight increase with the autoxidation of samples was determined by the weighing procedure (4).

Analytical Procedure

The detection and determination of the quantity of antioxidant radicals produced in the autoxidation of samples containing 2.00% by wt antioxidants were carried out at 20 C using an electron spin resonance (ESR) spectrometer (Japan Electron Optics Lab. Co., Tokyo, Japan; model JES-1X) in the 5 mm diameter quartz tubes for ESR. The antioxidants in the autoxidized samples were collected by washing with CCl_4 and determined with an IR spectrophotometer (a Shimadzu IR-27B apparatus) by the KBr

TABLE I

Effects of Ion Exchange Resins and Ethyleneimine Polymer (2% by wt) on the Induction Period in the Autoxidation of Methyl Linoleate

Sample	Exchange (functional) group	Type of ion	Induction period (hr) (ratio to control) Normal		Treated with H_2O_2	
IR 120B	$-SO_3M$	Na	51	(1.0)	50	(1.0)
IR 120B	$-SO_3M$	H	70	(1.4)	70	(1.4)
Dowex 50W	$-SO_3M$	H	74	(1.5)	73	(1.5)
IRC 50	$-COOM$	H	48	(1.0)	48	(1.0)
IRA 400	$-N(CH_3)_3X$	Cl	51	(1.0)	50	(1.0)
IRA 400	$-N(CH_3)_3X$	OH	50	(1.0)	50	(1.0)
IRA 410	$-N\begin{matrix}(CH_3)_2X \\ C_2H_4OH\end{matrix}$	Cl	33	(0.7)	35	(0.7)
		OH	42	(0.9)	42	(0.9)
IRA 93	$-N(CH_3)_2$	OH	42	(0.9)	43	(0.9)
IR 45	$-N(R)_2$	OH	231	(4.7)	70	(1.4)
IR 45	$-NH(R)$	OH	231	(4.7)	70	(1.4)
IR 45	$-NH_2$	OH	231	(4.7)	70	(1.4)
Ethyleneimine polymer	$-C_2H_4NH-$	$-C_2H_4NH-$	305	(8.1)		
Control			49			

tablet method.

RESULTS AND DISCUSSION

Antioxidant Activity

The variation in weight gain with the autoxidation of ML in samples containing 2.00% by wt of the NH type of IER and EP is shown in Figure 1. These antioxidant activities were compared at the time (hr) required to gain 10 mg as the weight gain that was generally regarded as the end point of the induction period in all samples. These induction periods are shown in Table I.

The relative antioxidant activities of IER and EP to control were calculated from the comparison in these induction periods. IER without the NH group scarcely showed antioxidant activities. Therefore, it was clarified that these IER couldn't participate in the chain termination with the peroxy radicals in the autoxidation of ML, though the conjugated diene content in the autoxidized samples was largely different from the control, as shown in the companion paper. This result was well understood from the evidence that the treatment of IER with H_2O_2 had no effect on its antioxidant activity, and the IR spectra for these IER treated with H_2O_2 or recovered from the autoxidized samples looked the same as each original IER. Also, the antioxidant radical formation due to the IER was not recognized in the autoxidation of ML and the treatment with H_2O_2. Antioxidant activities were recognized only in IR 45 and EP, with the NH group having the labile hydrogen. But the treatment of IR 45 with H_2O_2 made its antioxidant activity disappear. The antioxidant activities tended to increase linearly with the concentration of IR 45 or EP, as shown in Figures 2 and 3.

Therefore, the autoxidation of ML containing IR 45 or EP was retarded compared to the induction period of control by 91 or 174 hr per 1% by wt, respectively. The slope in the weight gain from the end of each induction period to the maximum weight gain wasn't affected by the IER, as shown in the value of 1.2 mg/hr for the samples with and without IER (Figs. 1 and 2). But the slope for the samples with EP decreased with its incremental additions, as shown in 0.57 mg/hr at 2.00% by wt, 0.46 mg/hr at 10.00% by wt, and 0.29 mg/hr at 30.00% by wt. This phenomenon might result from the slow participation of EP radicals into the free radical chain termination. The coupling reaction of EP radicals with peroxy radicals would be preferred at the autoxidation stage after induction because the reaction system was heterogeneous only until the end of the induction period. The added EP gradually melted at the autoxidation stage after the induction period and completely at the autoxidation stage over 120 mg weight gain. This conversion in the reaction system was likely induced by the increasing polarity of the autoxidized substrate with the accumulation of hydroperoxides. The presumption that the coupling of EP radicals with peroxy radicals induced the low slope in the weight gain was supported by the low slope and the low value in the peroxide value (PV), as shown in the companion paper and the disappearance of EP radicals at the autoxidation stage after its induction period. On the other hand, the maximum value in the weight gain was almost the same in the samples with and without all these antioxidants. This fact likely showed that the amount of oxygen absorbed in the autoxidation of ML was almost the same regardless of the existence and the sort of antioxidants. These antioxidant activities were confirmed by the results of PV, IR, and UV spectra, etc., for the autoxidized samples in the companion paper.

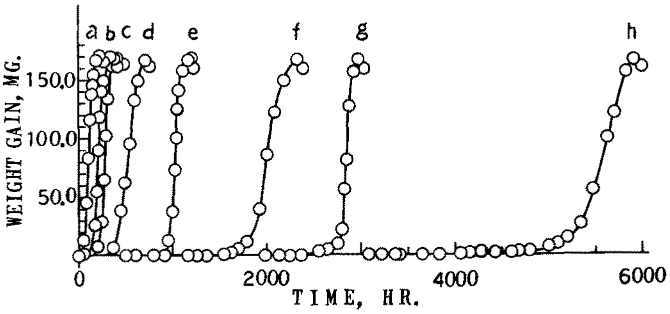

FIG. 2. Concentration effects of ion exchange resins and ethyleneimine polymer on weight gain in the autoxidation of methyl linoleate. (a) Control. (b,c,e,g) 1, 2, 10, and 30% by wt of Amberlite IR 45. (d,f,h) 2, 10, and 30% by wt of ethyleneimine polymer.

Termination Mechanism

The autoxidation mechanism of olefins has been generally proposed as follows (5,6):

$$RH + O_2 \rightarrow R\cdot + \cdot OOH \tag{1}$$

$$R\cdot + O_2 \rightarrow ROO\cdot \tag{2}$$

$$ROO\cdot + RH \rightarrow ROOH + R\cdot \tag{3}$$

$$ROOH \rightarrow RO\cdot + \cdot OH \tag{4}$$

$$RO\cdot + RH \rightarrow ROH + R\cdot \tag{5}$$

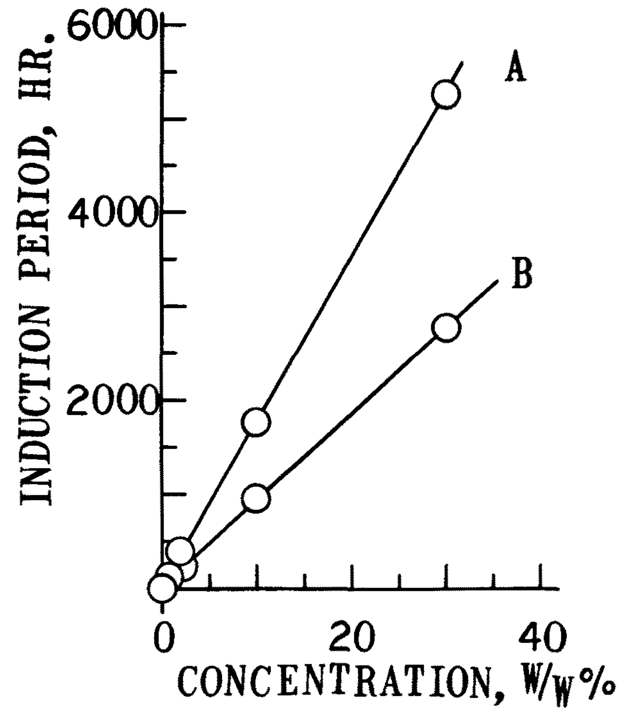

FIG. 3. Change of the induction period with the concentration of ethyleneimine polymer (A) and Amberlite IR 45 (B).

Various termination reactions are induced by the coupling and the disproportionation of free radicals. (6)

On the contrary, the termination mechanism of amino type antioxidants in homogeneous reaction systems has been proposed as follows (7-12):

$>NH + ROO\cdot \rightarrow >N\cdot + ROOH$ (7)
$>N\cdot + ROO\cdot \rightarrow >NOOR$ (8)
$>N\cdot + ROO\cdot \rightarrow >NO\cdot + RO\cdot$ (9)
$>NO\cdot + R\cdot \rightarrow NOR$ (10)

The color of IR 45 and EP was recognized to change from white to yellow with the autoxidation of ML. After the color no longer changed, quick elevation in the weight gain was observed. Also, the original IR 45 treated with H_2O_2 assumed a yellow color before addition. These color changes apparently result from the antioxidant radical formation. The IR spectra of original and recovered antioxidants from the autoxidized samples containing IR 45 and EP were observed. These spectra showed the decrease in the NH group at 3310 cm^{-1}, and the increase in the nitroxide group and its radical at 1750 and 1690 cm^{-1} for IR 45 and at 1788 and 1695 cm^{-1} for EP. This result suggests the formation of imino radicals owing to the hydrogen transfer from the NH group, and the transformation of imino radicals into nitroxide radicals as the consequence of the antioxidant abilities in IR 45 and EP. Still, the treatment of IR 45 with H_2O_2 gave the same change in IR spectra as recognized in the recovered antioxidants from the autoxidized samples containing the original IR 45. But IR 45 treated with H_2O_2 no longer changed in the autoxidation of ML. The variation of NH and NO groups with the autoxidation of ML was calculated from the IR spectra and shown in Figure 4. The decrease of the NH group was large, especially in the induction periods, but almost not recognizable at the autoxidation stage after the induction periods. Therefore, it was confirmed that the antioxidant activities of IR 45 and EP resulted from the hydrogen transfer from the NH group (Eq. 7). Here the analyses of IR spectra for EP were made on the unmelted separated substance in the autoxidized substrate.

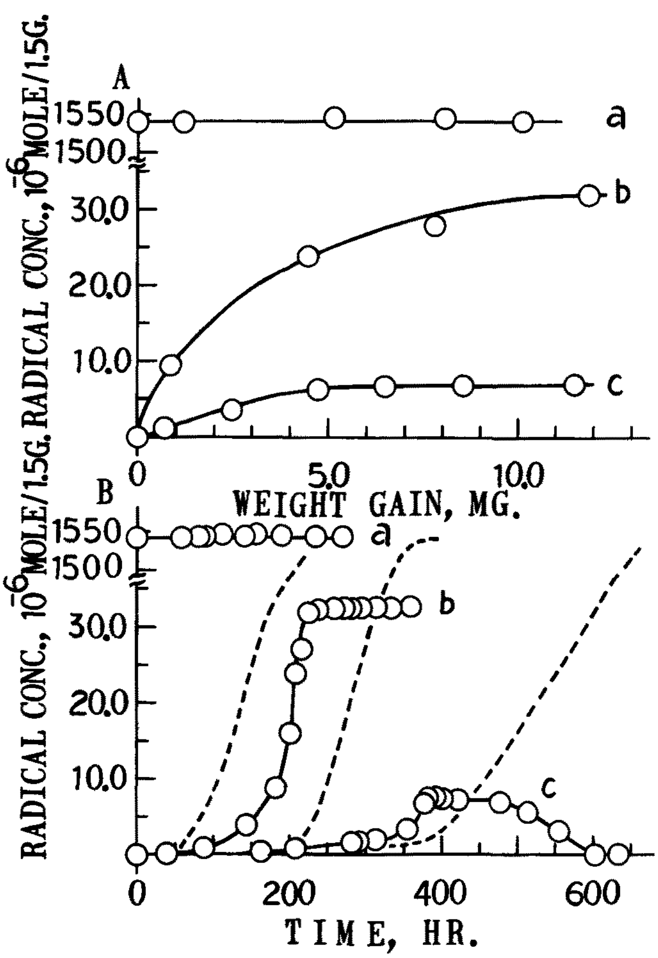

FIG. 4. Quantitative change of the functional groups of ion exchange resins and ethyleneimine polymer with the autoxidation of methyl linoleate. (A) Diminution of NH at 3340 cm^{-1} in IR spectra of Amberlite IR 45 treated (a) and untreated (b) with H_2O_2, and at 3310 cm^{-1} in IR spectra of ethyleneimine polymer (c). (B) formation of NO at 1750 (a) and 1690 cm^{-1} (b) in IR spectra of IR 45, and at 1788 (c) and 1695 cm^{-1} (d) in IR spectra of ethyleneimine polymer.

The ESR signals for IR 45 and EP radicals produced in the autoxidation of ML are shown in Figure 5. The treatment of IR 45 with H_2O_2 gave the same ESR signals as in the untreated material present in the autoxidation substrate. These signals were found to split into the three peaks under the influence of the nitrogen atomic nuclei, though its hyperfine splitting wasn't clear. The variation of the antioxidant radical concentration with the autoxidation of ML is shown in Figure 6.

IR 45 treated with H_2O_2 didn't show any change in the antioxidant radical concentration. On the other hand, the addition of IR 45 resulted in the appearance of a large amount of the anitoxidant radical, especially in its induction period, and thereafter its radical concentration arrived at a constant value. In the addition of EP, the antioxidant radical produced had arrived at the constant value by the end of the induction period, but subsequently gradually decreased. The decrease in the EP radical concentration was likely owing to the transformation from a heterogeneous to homogeneous reaction system as described above, because the coupling reaction of the antioxidant radicals with peroxy radicals might be preferred in the latter. From the viewpoint that the NO formation was observed at a later autoxidation stage than the increase of the antioxidant radical concentration and that it gradually increased even after the antioxidant radical concentration arrived at the

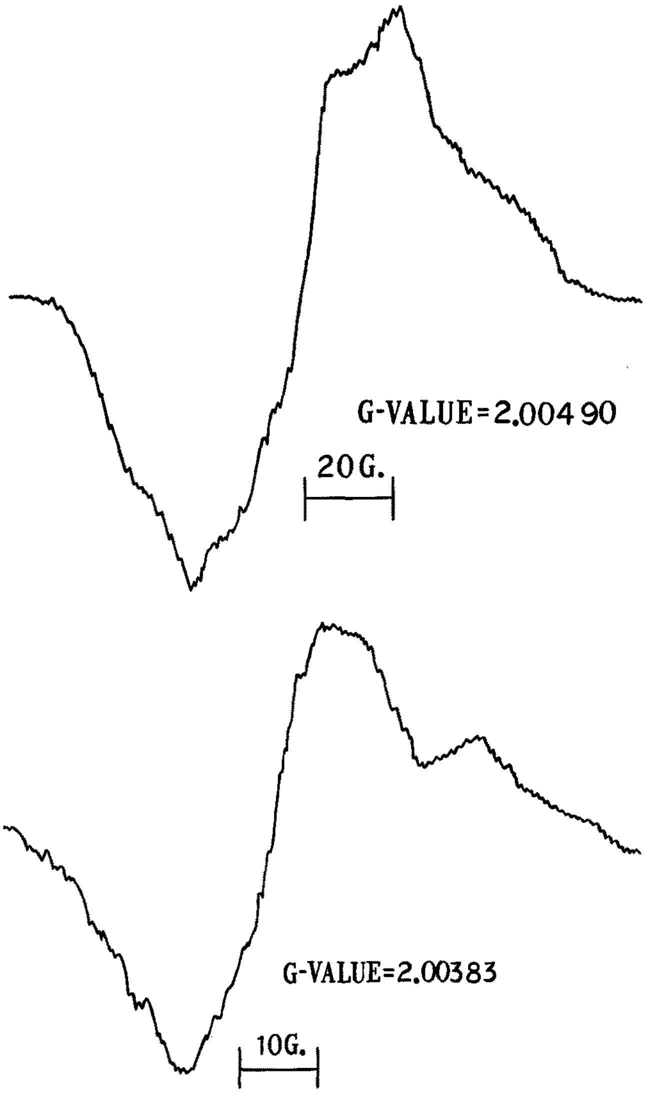

FIG. 5. Electron spin resonance spectra of the free radicals due to Amberlite IR 45 (A) and ethyleneimine polymer (B) produced in the autoxidation of methyl linoleate. Autoxidation degree of the A sample: 11.9 mg in the weighing procedure. Autoxidation degree of the B sample: 8.6 mg in the weighing procedure.

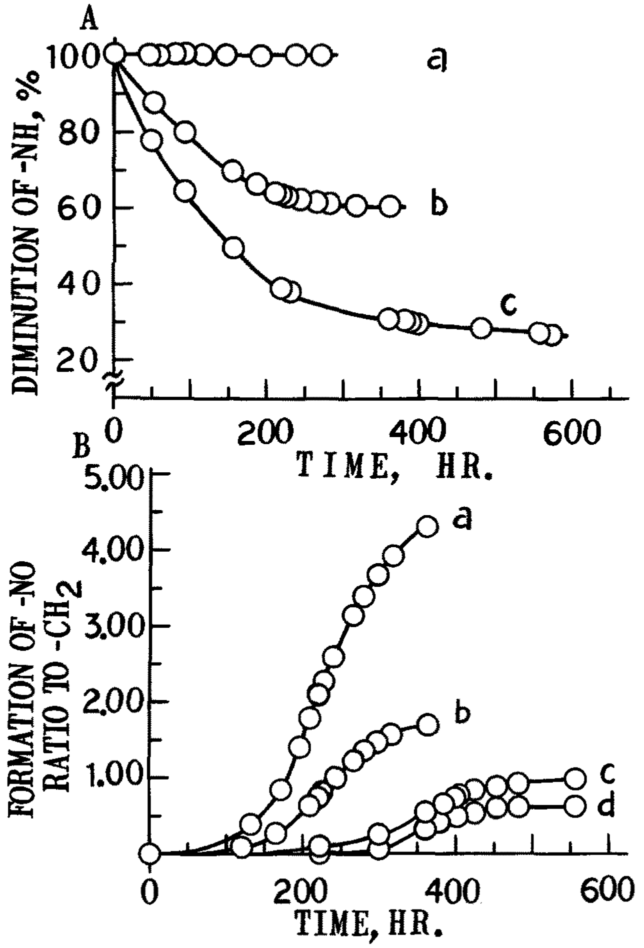

FIG. 6. Change of free radical concentration due to ion exchange resins and ethyleneimine polymer with weight gain (A) and with lapses of time (B) in the autoxidation of methyl linoleate. (a,b) Amberlite IR 45 treated and untreated with H_2O_2. (c) Ethyleneimine polymer; the dotted lines in B show the change of weight gain in the weighing procedure.

constant value, as shown in Figures 4 and 6, it is evident that the antioxidant radicals produced at the initial autoxidation stage were imino radicals. At any rate, these results showed that the antioxidant radicals were stable and couldn't effectively participate to lengthen induction periods, as shown by the unchanged concentration of the antioxidant radicals produced by the treatment of IR 45 with H_2O_2, the simple increase of IER and EP radical concentration to arrive at the constant value within these induction periods, and the simple increase of the NO formations. Moreover, comparison of the maximum weight gains with the control showed that the slow participation of EP radicals into the chain termination at the autoxidation stage subsequent to the induction period, inducing the low slope in the weight gain, resulted from the coupling reaction of imino radicals with peroxy radicals. Nitroxides and its radicals in IR 45 and EP may be produced largely by the direct oxidation of imino radicals, at least in the autoxidation stage, to explain the correlation between weight gains and PV as shown in the companion paper, because equation 9 couldn't explain this correlation. The possible effects of IR 45 and EP on the decomposition of autoxidized ML and t-butyl hydroperoxide were also considered. But the catalysis of IR 45 for the decomposition of these hydroperoxides wasn't observed. In the addition of EP, a small catalytic effect was recognized, especially in the decomposition of the autoxidized ML in comparison with control. But catalysis of EP was much smaller than the amino type of antioxidants in homogeneous reaction systems, such as phenothiazine. Therefore, the effects of IR 45 and EP on the decomposition of hydroperoxides produced in the autoxidation of ML were thought negligible, as shown in the similar change of PV to control in the companion paper. All these results show that the antioxidant activities of reagents containing radical species in heterogeneous reaction systems are negligible, but that the use of antioxidants with labile hydrogen, such as the NH group, is effective even in a heterogeneous reaction system. This type of antioxidant possibly might be economically favorable because of its ability to undergo regeneration at a suitable time.

REFERENCES

1. Fukuzumi, K., and N. Ikeda, JAOCS 46:64 (1969).
2. Mehlenbacher, V.C., "The Analysis of Fats and Oils," Swift & Co., Chicago, IL, 1960, p. 586.
3. Griffith, O.H., and A.S. Waggoner, Accounts Chem. Res. 2:17 (1969).
4. Olcott, H.S., and E. Einset, JAOCS 35:161 (1958).
5. Pryor, W.A., "Free Radicals," McGraw-Hill Book Co., New York, NY, 1966, p. 290.
6. Bateman, L., Q. Rev. (London) 8:147 (1954).

7. Brownlie, I.T., and K.U. Ingold, Can. J. Chem. 44:861 (1966).
8. Howard, J.A., and E. Furimusky, Ibid. 51:3738 (1973).
9. Harris, L.A., and H.S. Olcott, JAOCS 43:11 (1966).
10. Harle, O.L., and J.R. Thomas, J. Am. Chem. Soc. 84:2930 (1962).
11. Thomas, J.R., Ibid. 82:5955 (1960).
12. Thomas, J.R., and C.A. Tolman, Ibid. 79:2973 (1957).

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