

# Preparation and Activity of Sterically Hindered Phenol Antioxidants for NR and SBR

M.T.Khorasani and G.R.Bakhshandeh Polymer Research Center of Iran , Tehran, I.R. of Iran

**Key Words:** antioxidant ,synthesis ,substituted groups ,high molecular weight ,activity.

## ABSTRACT

Antioxidants of 2[2,2,3,4,5,5 hexa methyl hexyl]-6- tert butyl -4- methyl phenol and 2[2,2,3,4,5,5 hexa methyl hexyl]-4,6, di-tert butyl phenol are synthesized.The efficiency of these antioxidants and 2,6-di-tert butyl -p-cresol (BHT) and 2,4,6-tri- tert butyl phenol (TTP) and styrenated-phenol (SP), have been studied by comparing physical and thermal properties(e.g, tensile strength ,elongation at break differential scanning calorimetry) ,of the related non-black NR and SBR.The work described in this paper shows that the activity depends on the substituted groups in the ortho and para position on phenol structures and the molecular weight of the antioxidants.

## INTRODUCTION

Phenolics ,amines ,organo sulfur and organo phosphorus compounds are well known antioxidants for natural and synthetic rubber.The molecular weights of such species tend to be relatively low, often leading to surface bloom and volatilization from the compound.The use of high molecular weight materials as antioxidants is also well known [1,2].However ,such rubber antioxidants are expensive to manufacture and are often dangerously volatile or have staining effects on rubber.Staining effects are particularly undesirable in the manufacture of white rubber [3].

Applications have been developed for synthesis of two rubber antioxidant compositions which are both non-volatile and non staining.These antioxidant compositions are synthesized from p-cresol,4-tertbutyl phenol ,isobutylene and 2,2,3,4,5,5- hexa methyl-3-hexene to yield 2[2,2,3,4,5,5 hexa methyl hexyl]-6- tert butyl-p- cresol (HMTC)and 2[2,2,3,4,5,5 hexa methyl hexyl]-4,6-di-tert butyl phenol (HMDC).

## EXPERIMENTAL

### Materials

Para-cresol,isobutylene,4-tert butyl phenol ,2,6-di-tert butyl-p-cresol ,2,4,6-tri-tert butyl phenol ,

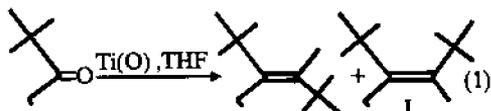
styrenated-phenol ,tert butyl methyl ketone were purchased from Merck Chemical Company, and 2,2,3,4,5,5 hexa methyl-3-hexene was prepared according to published procedures.With the exception of isobutylene, they were all purified according to known procedures[4,5].

Six masterbatches containing 100 phr pale crepe, 1 phr stearic acid ,5phr zinc oxide,25 phr calcium carbonate and 5 phr titanium oxide,were used in the physical experiments.

Six masterbatches containing 100 phr styrene-butadiene rubber (SBR 1502),5 phr zinc oxide ,1 phr stearic acid ,50 phr china clay ,50 phr calcium carbonate, 3 phr dioctyl phthalate and 5 phr titanium oxide were used in the thermal experiments. Except pale crepe, all materials were obtained from the Bayer Company.

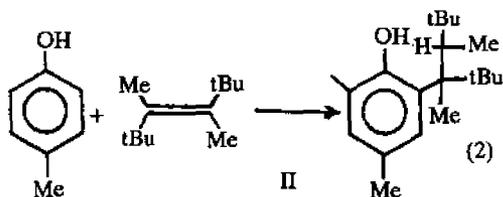
### Synthetic Procedures

2,2,3,4,5,5 Hexa methyl-3-hexene(I) was synthesized from tert butyl methyl ketone [6,7].This reaction has been postulated to occur as shown in equation (1).



Synthetic methods for the substances II- V are given below:

- 2[2,2,3,4,5,5 Hexa methyl hexyl] -p- cresol: according to the present method, 108 g(1 mole) of p-cresol in a 1 liter three necked flask fitted with a condenser ,in N<sub>2</sub> atmosphere ,was condensed by the dropwise addition of 168 g(1 mole) of 2,2,3,4,5,5 hexa methyl -3- hexene at 140°C at the rate of 3.7g per minute.The condensation reaction was catalyzed by the addition of 3.25g of sulfuric acid(96%).Upon cooling ,the reaction mixture containing yellow oil was removed by dissolving in 500 ml of benzene.The benzene solution was washed with three 200 ml portions of 2% sodium hydroxide solution and then with water until the washings were neutral to litmus.The washed benzene solution was dried over anhydrous sodium sulfate and freed of solvent by distillation at approximately 30 mm. pressure. There was a 60% yield of 2[2,2,3,4,5,5 hexa methyl hexyl ]-p- cresol, with a boiling point of 191°C at 10 mm.The reaction proceeds as shown in equation (2).



- 2[2,2,3,4,5,5 Hexa methyl hexyl]-6- tert butyl-4- methyl phenol:136g (0.5 mole) of II were butylated ,into the pyrex reaction vessel used for most of cresol alkylations involving gaseous olefins which is shown in Figure 1, by adding 56g (1 mole) of isobutylene at 100°C and for 4.5 hr.This reaction was catalyzed through the addition of 1.5g of sulfuric acid (96%).Upon cooling the reaction mixture solidified and was removed by dissolving in 200 ml of benzene.The benzene solution was washed with three 100 ml. portions of 2% sodium hydroxide solution and then with water until the washings were neutral to litmus.The washed benzene solution was dried over anhydrous sodium sulfate and freed of solvent by distillation at approximately 30mm pressure.

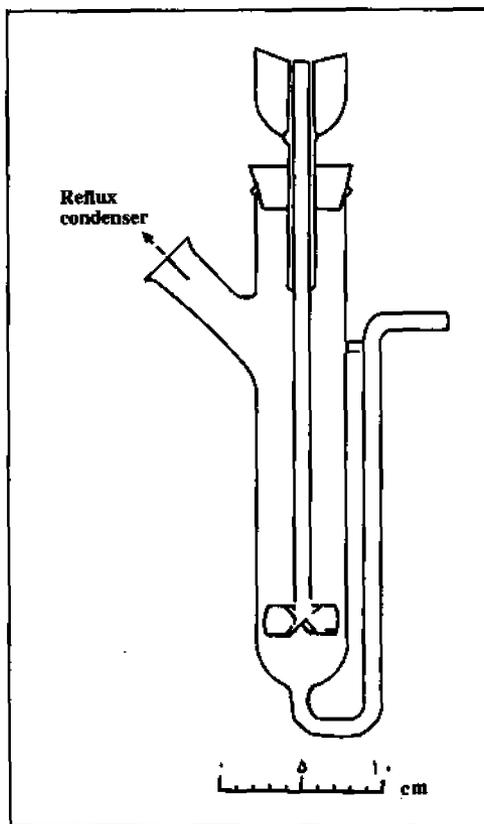
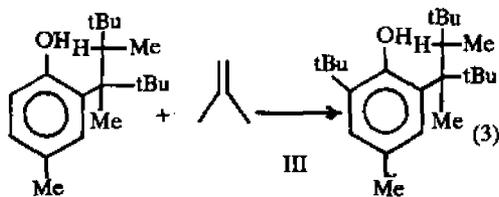


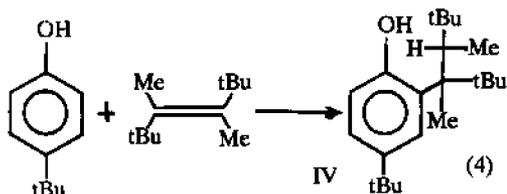
Figure 1:Reaction vessel for p-cresol alkylation

The benzene free residue was distilled at 10 mm pressure ,in a flask equipped with a vigreux column.The fraction boiling at 212°C weighed 70g and cooled to give a white solid material(II).The reactions are postulated to proceed as shown in equation (3).

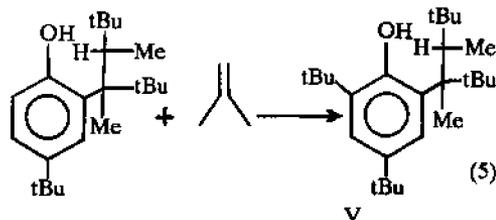


- 2[2,2,3,4,5,5 Hexa methyl hexyl]-4-tert butyl phenol:138g (1 mole) of 4-tert butyl phenol were condensed by the dropwise addition of 168g (1 mole) of 2,2,3,4,5,5 hexa methyl-3-hexene at 150°C at the rate of 6-g per minute.

The condensation reaction was catalyzed by the addition of 3.5g of sulfuric acid (96%). After usual work-up, there was a 50% yield of 2[2,2,3,4,5,5 hexa methyl hexyl]-4-tert butyl phenol(IV). This composition has a boiling point of 205°C at 10 mm. The reaction proceeds as shown in equation (4).



- 2[2,2,3,4,5,5 Hexa methyl hexyl]-4,6-di-tert butyl phenol:153g (0.5 mole) of IV were butylated by adding 56g (1 mole) of isobutylene at 120°C for 4.5 hr. This reaction was catalyzed through the addition of 1.5g of sulfuric acid (96%). The fraction boiling at 221°C at 10 mm pressure weighed 140g and cooled to give a yellow solid material (V). The reaction is postulated to proceed as shown in equation (5).



### Formulations

The rubbers were compounded according to the formulations given in Tables 1 and 2 using a laboratory 45 cm two-roll mill according to ASTM D3182. The amounts of antioxidants were optimized by use of resistance to heat aging.

### Measurements

Identification of synthetic antioxidants was carried out by <sup>1</sup>H-NMR (Varian, 90 MHz Instrument) and

a solution of 0.1g pure antioxidant in 0.5ml CDCl<sub>3</sub> was used.

Physical tests were conducted for all molded compounds after molding and exposure of press cured samples in a circulating air oven at 80°C for up to 24 hr.

Table 1: Formulation for natural rubbers

Material ,phr	1	2	3	4	5	6
Pale crepe	100	100	100	100	100	100
Stearic acid	1	1	1	1	1	1
Zinc Oxide	5	5	5	5	5	5
Calcium Carbonate	25	25	25	25	25	25
Titanium Oxide	5	5	5	5	5	5
Sulfur	2.25	2.25	2.25	2.25	2.25	2.25
TMTD	0.25	0.25	0.25	0.25	0.25	0.25
MBT	0.5	0.5	0.5	0.5	0.5	0.5
SP	-	1	-	-	-	-
BHT	-	-	1.5	-	-	-
TTP	-	-	-	1.2	-	-
HMTC	-	-	-	-	1	-
HMDC	-	-	-	-	-	1

Tensile strength, modulus, and elongation were determined according to ASTM D412 using Instron 6025 with 10KN load cell tensile tester at a crosshead speed of 50 cm/min.

Table 2: Formulation for SBR rubbers

Material ,phr	1	2	3	4	5	6
SBR 1502	100	100	100	100	100	100
Zinc Oxide	5	5	5	5	5	5
Stearic acid	1	1	1	1	1	1
China clay	50	50	50	50	50	50
Calcium Carbonate	50	50	50	50	50	50
Diocyl phthalate	3	3	3	3	3	3
Camaron indene resla	4	4	4	4	4	4
Wax	2	2	2	2	2	2
Titanium oxide	5	5	5	5	5	5
MBTS	1.5	1.5	1.5	1.5	1.5	1.5
TMTD	0.3	0.3	0.3	0.3	0.3	0.3
S	2	2	2	2	2	2
SP	-	1	-	-	-	-
BHT	-	-	1.5	-	-	-
TTP	-	-	-	1.2	-	-
HMTC	-	-	-	-	1	-
HMDC	-	-	-	-	-	1

Shore A hardness tests were determined for samples after molding, using a hand-held Shore A durometer.

Cure characteristics, which include scorch time, cure rate, and torque values, were measured over a 20 min period at 141°C for NR and 165°C for SBR using a Zwick torsional thrust vulcameter.

The SBR compounds were subjected for differential scanning calorimetry measurements. A DSC (Stanton 780 model) was used in the present investigation. Thermographs of vulcanized SBR were determined between room temperature and 500°C. A heating rate of 10°C per min, was used in all cases. An oxygen atmosphere was provided and the flow of the gas was kept constant at 0.2 liters per minute. At least three thermographs were obtained for each sample to ensure reproducibility. The heat of reaction values were calculated from the average areas.

## RESULTS AND DISCUSSION

### NMR Spectra

Figure 2 shows the NMR spectra of 2[2,2,3,4,5,5 hexa methyl hexyl]-6-tert butyl-p-cresol (HMTc). 2H ( $\delta$ :6.7 ppm) are in the aromatic range, suggesting a disubstituted benzene -C<sub>6</sub>H<sub>2</sub>-, the 3H ( $\delta$ :3.3ppm) have a shift expected for benzylic proton, giving CH<sub>2</sub>-C<sub>6</sub>H<sub>2</sub>-, 1H ( $\delta$ :4.3ppm) is phenolic proton, 34 H ( $\delta$ :1.3 and 2ppm) are tert butyl and branched tert butyl protons in the ortho position.

Figure 3 shows the NMR spectra of 2[2,2,3,4,5,5 hexa methyl

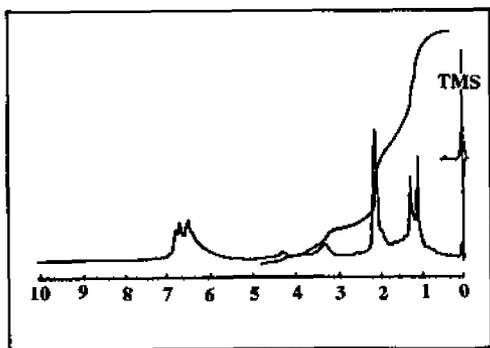


Figure 2: NMR spectra for 2[2,2,3,4,5,5 hexa methyl hexyl]-6-tert butyl-p-cresol (HMTc)

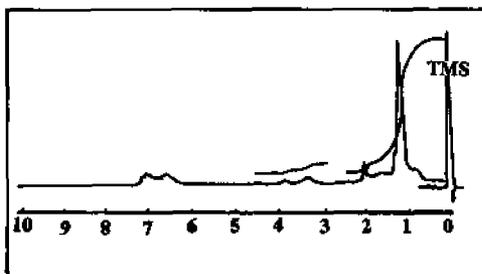


Figure 3: NMR spectra for 2[2,2,3,4,5,5 hexa methyl hexyl]-4,6-di-tert butyl phenol (HMDC)

4,5,5 hexa methyl hexyl]-4,6-di-tert butyl phenol (HMDC). 2H ( $\delta$ :7ppm) are in the aromatic range -C<sub>6</sub>H<sub>2</sub>-, 1H ( $\delta$ :4.5ppm) is phenolic proton, 43H ( $\delta$ :1.2ppm) are tert butyl on para and ortho position and branched tert butyl in the ortho position.

### Tensile Properties

The physical properties for NR and SBR compounds are given in Table 3 and 4 respectively. Figures 4 and 5 show the dependence of the relative change in elongation and tensile strength on aging time. It can be seen that these antioxidants protect NR vulcanizates against oxidative aging. Based on the ability of the antioxidant to retention of tensile strength and retention of percent elongation, the relative efficiencies of 5 antioxidants in NR follow the depending order:

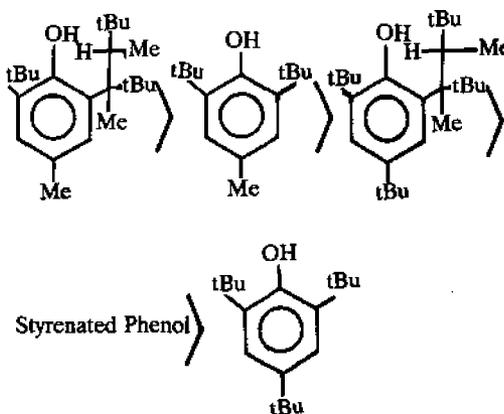


Table 3: Physical properties of NR rubber compounds from Table 1

Properties	1	2	3	4	5	6
Vulcanization at 141°C ,min	4.66	4.67	4.87	4.87	4.77	4.85
Scorch ,min	2.22	2.35	2.06	2.12	2.10	2.17
Minimum torque (lb/in)	3.12	3.56	2.88	3.19	3.11	3.04
Maximum torque (lb/in)	30.39	29.65	29.53	29.81	29.67	29.72
Modulus 300% MPa	3.47	3.53	3.65	3.51	3.8	3.62
Tensile strength at break ,MPa	20.56	21.76	22.25	21.10	22.27	21.92
Elongation ,%	605.4	632.6	642	622.3	661	635
Hardness ,Shore A	51	51.5	50.7	51.5	51	51
Durometer						
Resilience %	85	82	82	83	84	84

Table 4: Physical properties of SBR rubber compounds from Table 2

Properties	1	2	3	4	5	6
Vulcanization at 165°C ,min	11.5	12.23	12.55	11.9	12.7	12.67
Scorch ,min	2.03	2.29	2.61	2.21	2.27	1.96
Minimum torque (lb/in)	7.42	7.78	7.42	7.81	7.56	7.8
Maximum torque (lb/in)	51.88	49.85	46.82	50.26	44.94	42.75

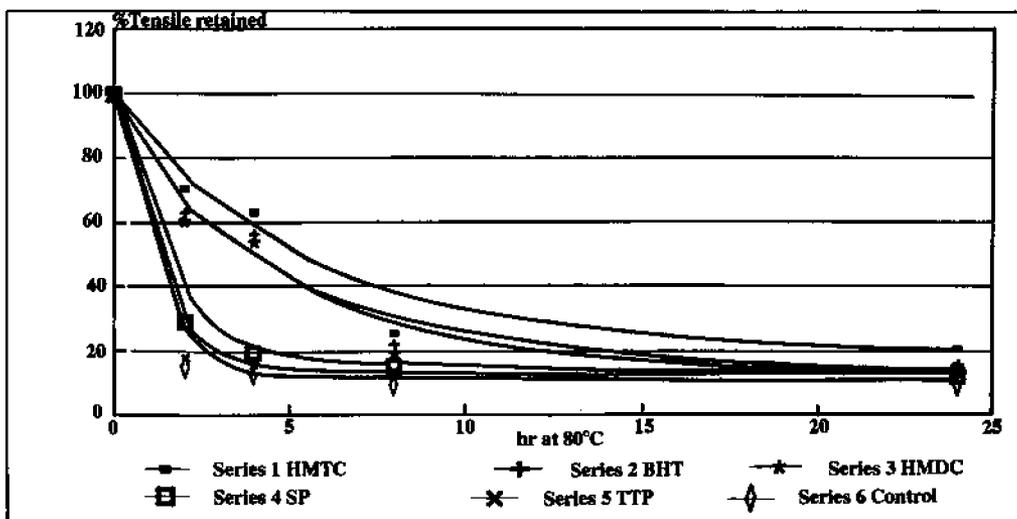


Figure 4: Tensile strength retained versus heat aging time for 24 hr at 80°C

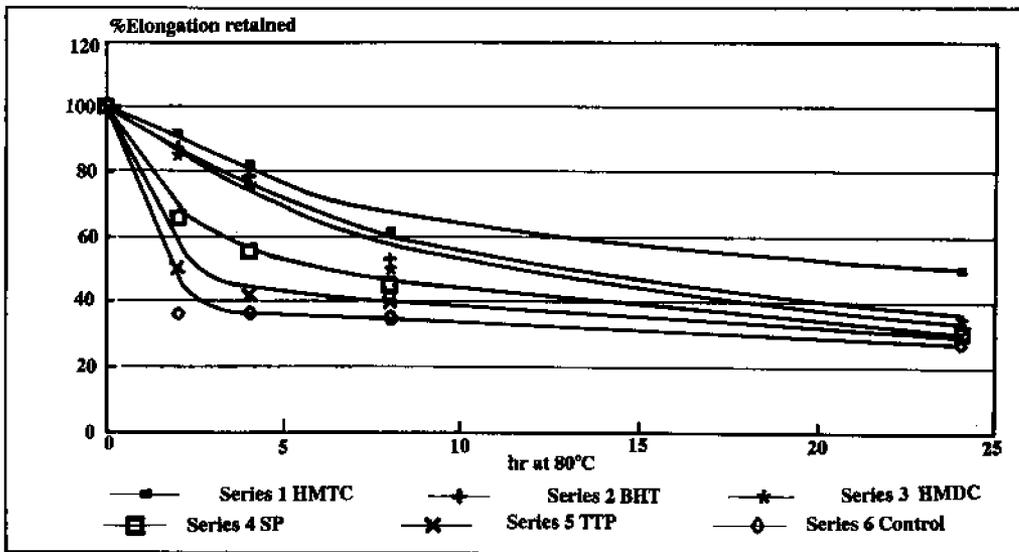


Figure 5: Elongation retained versus heat aging time for 24hr at 80°C

#### Antioxidant Evaluation by DSC

Oxidation processes occur at temperatures considerably lower than those at which thermal degradation is initiated in an inert atmosphere. The concept for calorimetric evaluation of antioxidant effectiveness is based on the ability of a given antioxidant to inhibit and/or reduce the magnitude of the oxidative exotherm [8].

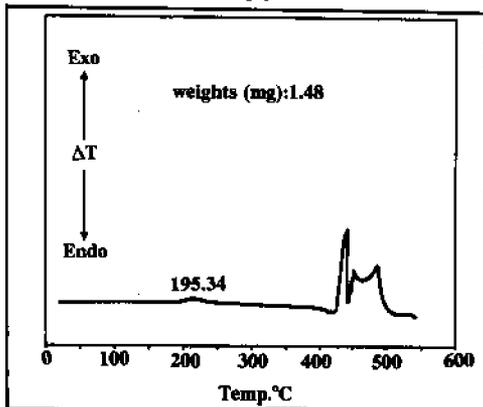


Figure 6: Thermograph for vulcanized SBR in oxygen (control)

Figure 6 shows the DSC thermograph for the oxidation of SBR that had no antioxidants. The profile shows two major exothermic events. The first exotherm reaction occurs at 195.34°C and the second occurs at 422.41°C.

A problem in such studies is construction of the baseline to allow calculations of enthalpy under each exotherm. Values reported for enthalpy can only be considered as estimates.

Enthalpy values were determined for the first major exotherm. These values and temperatures where oxidation reaction occurred are given in Table 5.

Table 5: DSC Analysis of SBR containing antioxidant

Antioxidant	Peak temp. °C	6H J/g
HMTc	205	210.75
BHT	199.43	337.33
HMDC	198.81	368.87
SP	197	384.13
TTP	196.84	405.89
Control	195.34	438.58

Results indicate that the presence of antioxidant in rubber, reduces oxidation reaction and the efficiency depends on reduction of enthalpy of the oxidation reaction. The relative efficiency of five antioxidants in SBR follow the depending order as for NR.

Two opposed processes were seen to be important to the function of antioxidants. Antioxidant activity is a result first of the ability of the material to deactivate alkyl peroxy radicals and second of the tendency of the antioxidant radical to continue the kinetic chain [9].

### CONCLUSIONS

Based on the data reported in this paper, it is evident that there is a good deal of information on the relationship between the antioxidant activity of phenols and their structures and molecular weights. The main conclusions may be summarized as follows:

- Electron releasing groups (e.g. methyl, tert butyl) in the ortho and para positions markedly increase antioxidant activity.
- Branched ortho alkyl groups considerably increase antioxidant activity, where as such groups in the para position decrease it.
- High molecular weight antioxidants often do not lead to surface blooming and volatilization from the compound, hence, increases antioxidant activity in rubber.

### ACKNOWLEDGMENT

We would like to thank Dr.A.A.Katbab (Amirkabir University of Technology), Dr.M.H. Rafiee (University of Tehran) and IranTire Co. for their helpful comments and discussions.

Date received: 17th February 1992



- [1]Badran B.M., Younan A.F., Ismail M.N and Shehata A.B., *Elastomerics*, Vol 3(1990).
- [2]Shelton J.R., *Rubber Chem. Technol.* 45,359 (1972).
- [3]Studebaker M.L., Beatly J.R., *Rubber Chem. Technol.* 45,450 (1972).
- [4]Perrin D.D. and Armarego N.L.F., in "Purification of Laboratory Chemicals", Third Edition, Pergamon Press, New York (1988).
- [5]Tatchell A.R. et al., *Vogel's Text Book of Practical Organic Chemistry*, 5th Ed. Longman Inc, New York, NY (1989).
- [6]McMurry J.E., Fleming M.P., Kees K.L., Krepski L.R., *J. Org. Chem.* 43,5255 (1978).
- [7]Lenoir D., Malwitz D and Bernd Meyer, *Tetrahedron Letters*, 25,2965 (1984).
- [8]Brazier D.W., Dunlop Research Centre, Sheridan Park Research Community Mississauga, Ontario, Canada, *Rubber Chem. Tech.* 53, 479 (1980).
- [9]Scott G. "Atmospheric Oxidation and Antioxidants", 115, Elsevier, New York (1965).