

The Mechanism of Oxidative Degradation of ABS Resin. Part I. The Mechanism of Thermooxidative Degradation

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Synopsis

In this work the early stages of the thermal oxidation of ABS resin films for commercial utilization and purified samples were studied by means of infrared spectroscopy. The film samples were submitted to thermal oxidation in a Gear oven at 70–90°C. During the aging in the Gear oven the nitrile and phenyl absorbance did not change, but oxidative products containing hydroxyl or carbonyl groups were produced rapidly, and the butadiene content decreased gradually. Two parts of the oxidative reaction were easily distinguished by analysis of the degradation procedure in the differential method and in the half-time method. An activation energy of 10 kcal./mole or less was obtained for the initiation process, involving mainly the formation of hydroperoxides induced by radical formation, which was apparent in the commercial samples, whereas a value of 10–20 kcal./mole was obtained for the subsequent process, initiated by the decomposition of the hydroperoxides, which induces chain-carrier reactions. A reaction scheme is proposed, and kinetic expressions are developed therefrom. These expressions explain the experimental results very well.

Introduction

Although the thermal oxidation of elastomeric high polymers has been studied extensively, there is little literature concerning the subject of oxidation in the acrylonitrile–butadiene–styrene copolymer. It was known that the physical properties, especially elongation and impact strength, of this material aged in a Gear oven at 70–90°C. in normal atmosphere show conspicuous deterioration. The effects were recognized to be due mainly to chemical changes, brought about through thermochemical reactions, that were greater than the physical changes on the material surface (notch effect, etc.).

This paper presents data on thermooxidative degradation of ABS resin at low temperatures, studied by means of infrared absorption spectroscopy. A thermooxidative degradation mechanism of the resin is proposed.

Experimental

For the purpose of removing additives, especially the stabilizer, the commercial ABS resins, manufactured by five resin makers, were purified by being dissolved in acetone and precipitated by methanol. Then they were submitted to elemental analysis, and the resin compositions were calculated, as indicated in Table I, on the assumption that the acrylonitrile part was

TABLE I
Compositions of ABS Resin

Polymer	Analysis, %			Composition, %		
	A	H	N	Acrylo- nitrile	Butadiene	Styrene
A	85.01	7.71	7.11	27.0	17.0	56.0
B	86.12	8.04	5.72	21.7	23.2	55.1
C	85.28	8.07	6.54	25.0	26.0	49.0
D	84.60	8.34	6.92	26.0	34.9	39.1
E	85.05	8.74	5.27	20.3	45.0	34.7

C_3H_3N , butadiene part was C_4H_6 and styrene part was C_8H_8 . The samples were named A, B, C, D, and E in order of increasing butadiene content. The film samples were made by compression-molding at 175–180°C. The preheating time was 4 min.; the compression time, 3 min. Films of 0.02–0.10 mm. in thickness were obtained.

Infrared spectra of the films were recorded with a Shimadzu-seisakusho Co., Ltd., IR-27 infrared spectrophotometer. The absorbance of the absorption bands in some regions were obtained by the baseline method described by Wright¹ or by the method of Heigl et al.²

Variation in film thickness was corrected to 0.1 mm., except for the butadiene absorbance calculation, which was based on the proportion of the absorbance at 6.9 μ to the thickness because of increasing background around the region below 6.0 μ , caused by heat degradation of the film.

The films were oxidized in forced-draft ovens for 1600 hr. at 70°C., for 900 hr. at 80°C., and for 400 hr. at 90°C. Oxidation was interrupted frequently for IR spectroscopy.

Results and Discussion

The course of the oxidative degradation of ABS resins was observed at the three temperatures 70, 80, and 90°C. Table II shows the absorption bands found in unoxidized resin; these assignments may be found in many publications.^{3–12}

Prior to oxidative degradation the spectra of the original film samples were obtained. A typical spectrum, that of purified sample B, is shown in Figure 1.

The effects of temperature on the rate of formation of carbonyl and hydroxyl groups or on the extinction of butadiene in ABS resins in air were

TABLE II
Infrared Spectra of ABS Resin

Polymer	Absorption band, μ	Assignment
Unoxidized	3.2 shoulder	C—H stretching of phenyl group
	3.31	C—H stretching or phenyl group
	3.42	ν_{as} CH ₂
	3.5 shoulder	ν_s CH ₂
	4.45	CN
	5.1–5.65	Mono-sub. of phenyl group
	5.95	Trisub. $\nu_{C=C}$, <i>trans</i> $\nu_{C=C}$
	6.2, 6.25 shoulder	Phenyl group
	6.7	CH ₂ , phenyl group
	6.85	CH ₂ , phenyl group
	7.3–8.45	C—H bending, CH ₂ , phenyl group
	8.65, 9.35, 9.7	Phenyl group
	10.3	<i>trans</i> $\nu_{C=C}$
	10.9	1,2-Butadiene, terminal vinyl δ CH
	11.9	Trisub. $\nu_{C=C}$
13.2, 14.3	Monosub. of phenyl group	
Oxidized	2.95	OH stretching
	5.8	C=O stretching

measured. For the rate data the spectral changes occurring in the film samples aged as the three temperatures were graphed; see Figures 2–5. The absorbances are corrected to 0.1 mm. thickness by using the proportion of absorbance to thickness. These data were used for verifying kinetic expressions that were derived from a proposed mechanism.

The infrared studies show the formation of a hydroxyl band at 2.95 μ and a carbonyl absorption band at 5.8 μ . The formation of these bands as the development of the oxidation is shown in Figures 2 and 3. Since the IR bands were broad and complex, the absorption of hydroxyl and carbonyl groups,

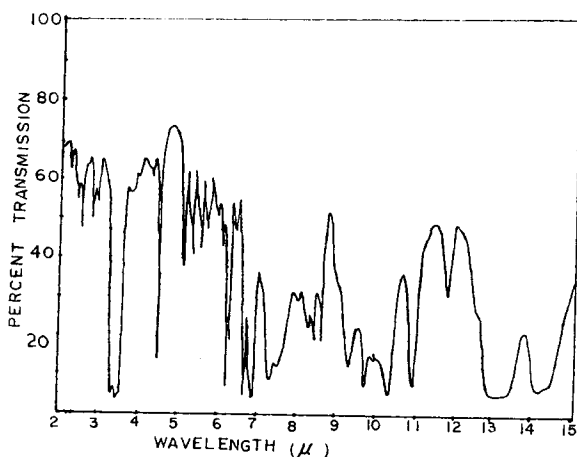


Fig. 1. Infrared spectrum of sample B, ABS resin film.

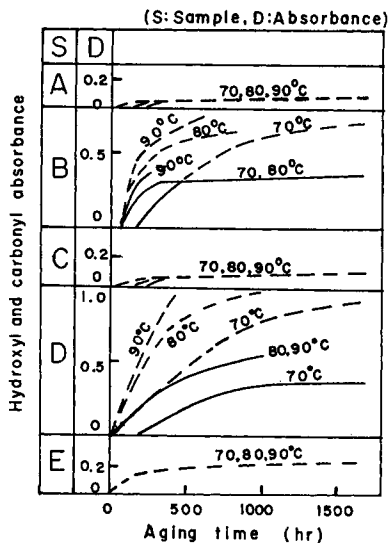


Fig. 2. Changes of 2.95μ (—) hydroxyl and (---) carbonyl absorbances for commercial samples. The hydroxyl absorbances in samples, A, C, and E are zero.

e.g., hydroxylic acid, hydroperoxides, carboxylic acid, aldehydes, ketones, and ester carbonyl groups, was studied.

The butadiene contents were indicated on the infrared spectra to be *trans*-1,4 form at 10.3μ , 1,2 form at 10.9μ , and *cis*-1,4 form at 14.5μ , having a little overlap with the phenyl group or the terminal vinyl group. Therefore these absorbances are not represented in the actual butadiene amount. It was found from Figures 4 and 5 that the degradation of the commercial samples was slow, whereas that of the purified samples was relatively rapid.

No changes in nitrile (4.45μ) and phenyl (5.14μ) absorption at each temperature were noticed in either the commercial or the purified samples. Moreover, at this stage of degradation the stretching frequency of the carbon-carbon double bond at 6.3μ scarcely changed in the absorbance during the low-temperature aging.

Kinetics Analysis

The rate constants and reaction orders were calculated by the differential method from the instantaneous rates of formation of the products discussed below.

For the hydroxyl or carbonyl bands in the infrared spectra the increasing ratio of absorbance D at arbitrary time t has been proposed as the following equation:

$$-dD/dt = K(D_{\max} - D)^n \quad (1)$$

where D_{\max} is the maximum absorbance, k is the reaction rate constant, and n is the reaction order. This equation may be written as

$$\log (-dD/dt) = \log k + n \log (D_{\max} - D) \quad (2)$$

Therefore, the instantaneous rates could be calculated from the graphs of the plot of $\log(-dD/dt)$ versus $\log(D_{\max} - D)$.

If the range of the $(D_{\max} - D)$ values is comparatively narrow, then, instead, $\log(-dD/dt)$ versus $\log D$ or $\log \Delta D$ versus $\log D$ could be regarded as approximately showing simple proportionality.

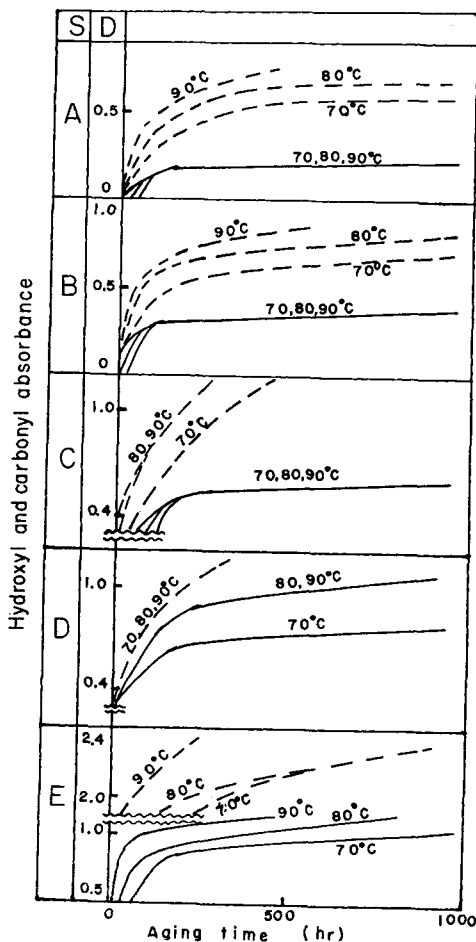


Fig. 3. Changes of 2.95μ (—) hydroxyl and (---) carbonyl absorbances for purified sample.

As mentioned above, this linear presentation, containing the differential elementary reactions for the thermooxidative degradation, is expected to bend at the point where the elementary reaction of rate-determining stage changes. Therefore, from this bent point the degradative reactions are distinguished, and D_{\max} can be obtained for each reaction. Thus, from Figures 2 and 3 the extinction coefficients of the series of reactions was calculated for hydroxyl and carbonyl groups, as indicated in Figures 6 and 7.1

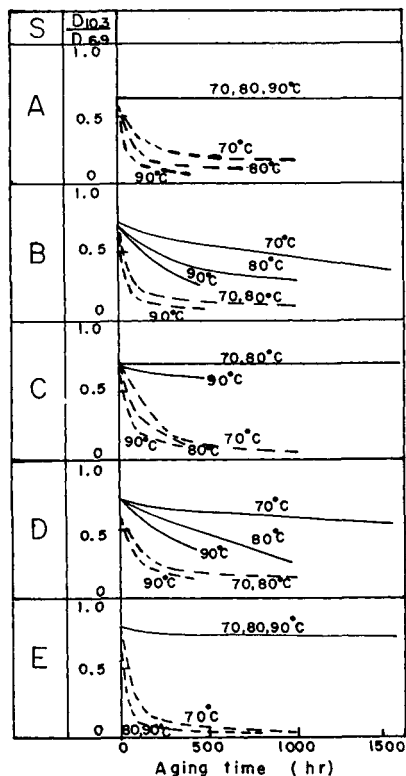


Fig. 4. Changes of 10.3μ *trans*-1,4-butadiene absorbance for (—) commercial and (---) purified samples.

The ΔD values were calculated by using the difference of absorbance after every 40 hr. of aging.

As may be seen, the commercial samples are distinguished by two parts divided by a crease, which appears in Figures 6 and 7; the purified samples show no such increases. The first part is called here part 1 and the second, part 2.

Then the D_{\max} obtained from Figure 6 and 7 were applied in eq. (2), and the reaction rate constant k and reaction order n were obtained. The constant k is measured as reciprocal hours.

From the slopes of Arrhenius plots of the logarithm of the reaction rate constant k versus the reciprocal absolute temperature $1/T$ the activation energies E were estimated. The average of these values is 10 kcal./mole or less for the first reaction of thermooxidative reactions and 10–20 kcal./mole for the subsequent process.

The half-time method also could be used for determining the activation energies. The following equation may be obtained from eq. (1) and the Arrhenius equation:

$$\ln t = \ln [1/A \ln D_{\max}/D] + E/RT \quad (3)$$

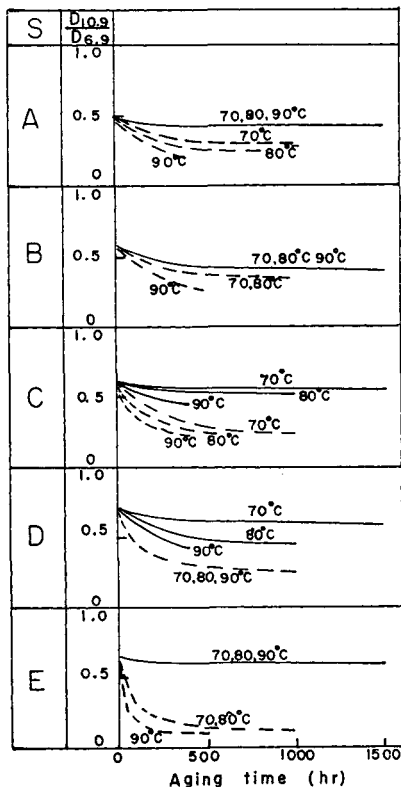


Fig. 5. Changes of 10.9μ 1,2-butadiene absorbance for (—) commercial and (---) purified samples.

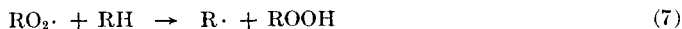
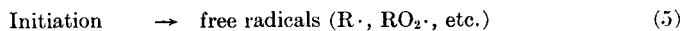
where A represents a constant. Now, if the half-time $t_{1/2}$ is defined as the time corresponding to the half-absorbance of D_{\max} , this equation becomes

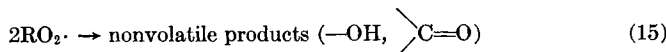
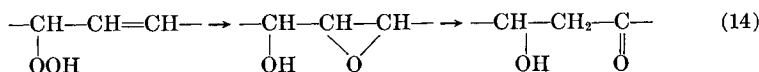
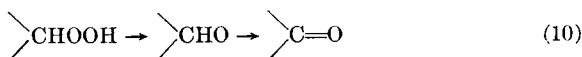
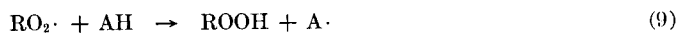
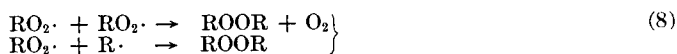
$$\ln t_{1/2} = A' + E/RT \quad (4)$$

where A' is a constant. Therefore the activation energies may be calculated from the slopes of the plots of $\ln t_{1/2}$ versus $1/T$. The plots for calculating the activation energies by the half-time method are shown in Figures 8 and 9. The values obtained are summarized in Table III.

The Reaction Scheme

To explain the results obtained, the following kinetic scheme has been proposed. The reactions listed below are assumed to be the predominant steps occurring during the thermal oxidation of ABS resin:





In this scheme R indicates a polymer backbone. Step (5) depicts a part of the formation of hydroperoxide.

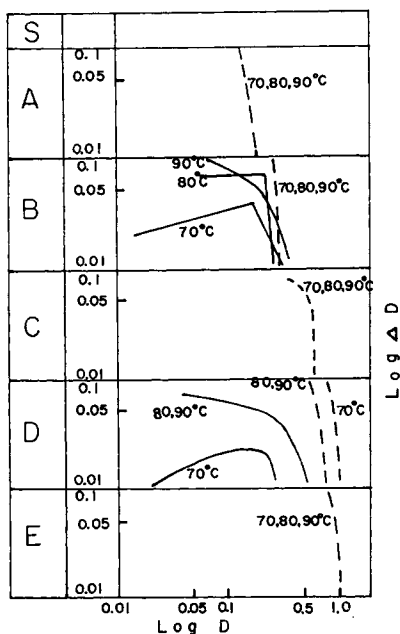


Fig. 6. Extinction coefficients of hydroxyl formation reactions shown by infrared spectra for (—) commercial and (---) purified samples.

The degradation of polymer is generally initiated by the formation of free radicals. The following three types of reaction are considered to be possible initiation reactions: direct scission of the weaker bond, finally producing a double bond, the hydrogen abstraction (i.e., abstraction of hydrogen from the C—H bond by atmospheric oxygen, giving hydroperoxide or its radical), and aging, when an impurity is in the polymer. The first type of initiation reaction did not seem to be possible in this case, according

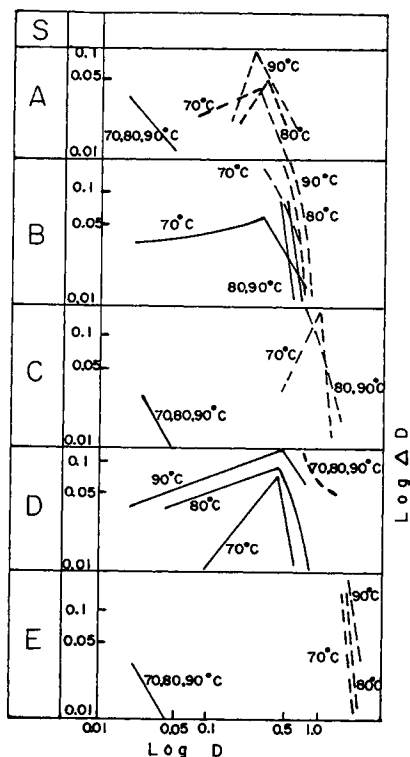


Fig. 7. Extinction coefficients of carbonyl formation reactions shown by infrared spectra for (—) commercial and (---) purified samples.

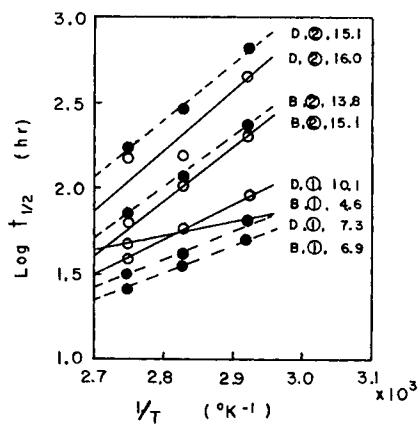


Fig. 8. Activation energies (kcal./mole) of oxide formation given by half-time method for commercial samples B and D: (O) OH; (●) CO. Numerals in circles signify parts 1 and 2.

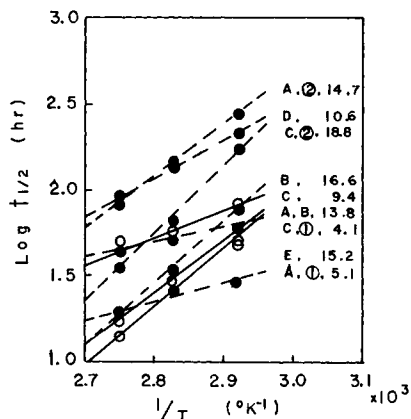


Fig. 9. Activation energies (kcal./mole) of oxide formation given by half-time method for the purified samples A to E: (O) OH; (●) CO. Numerals in circles signify parts 1 and 2.

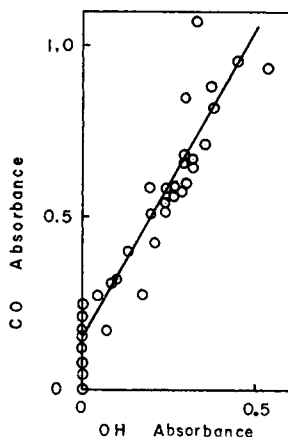
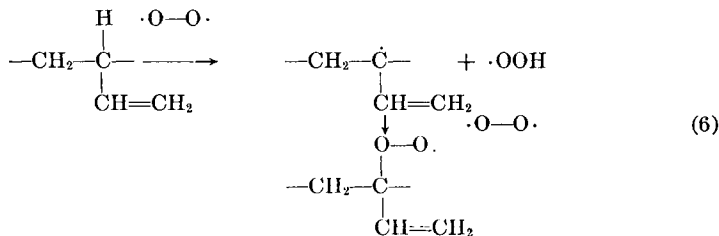


Fig. 10. Relation between hydroxyl and carbonyl formations through degradation in commercial samples.

to the infrared studies, since scarcely any double-bond formation in the low-temperature aging was recognized. In the oxidative degradation of polymer the second type, hydrogen abstraction by oxygen, was considered to predominate. As the ABS resin contains some double bonds, the C—H bond in the α -carbon position would be especially easy to oxidize.



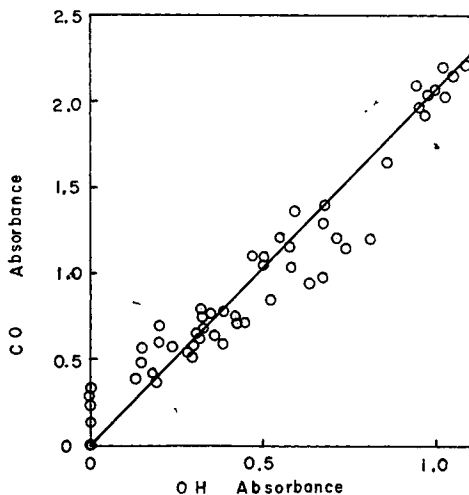


Fig. 11. Relation between hydroxyl and carbonyl formation through degradation in purified samples.

In the initiation reaction these radicals would be produced at first. They are very active ($R\cdot$, $RO_2\cdot$) and react easily, as indicated in steps (6) (7), and (8).

In the earlier oxidative degradation reaction for the commercial samples, the effect of the presence of stabilizer becomes apparent (step 9).

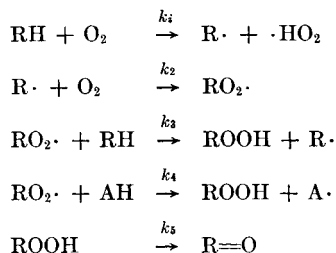
Because of the high reactivity of the radicals $RO_2\cdot$ with labile hydrogen (e.g., tertiary hydrogen or hydrogen attached to the α -methylene of the double bond in polymer)¹³ hydroperoxides gradually accumulated. At this point, since the hydroperoxide absorption is broad and poor,¹⁴ the hydroxyl absorbance (about 2.95μ) of the hydroperoxide would be scarcely observed. So Part 1 of the thermooxidative degradation was considered to be a series of reactions, steps (5)–(10) taking place before the formation of the hydroperoxide.

The part 2 reactions start from the hydroperoxide decomposition, which induces the autooxidative reaction, step (11). The radical $RO\cdot$ acts as a chain carrier, as indicated in steps (12) and (13), and then hydroxide and carbonyl products are produced. The chain-scission reaction effectively takes place at the methylene bond in the *trans*- (or *cis*-) 1,4-polybutadiene structure, which has the weakest carbon-carbon bond energy (38 kcal./mole)¹⁵ in this polymer; note step (13). When the hydroperoxide group was produced at the α -carbon position of the double bond, ozonide probably could be produced in step (14).

From Figures 2 and 3 the relations between hydroxyl and carbonyl absorbances at the same aging times are shown in Figures 10 and 11. In the earlier oxidative reaction for the commercial sample the carbonyl absorbance appeared more rapidly than the hydroxyl (Fig. 10), while in the later oxidative reaction both absorbances increased almost proportionally in both the commercial samples and the purified samples.

On the basis of the scheme and assumptions given above the course of the formation of oxidative products is considered to be as given below.

First of all, part 1 is assumed to contain the following kinetic scheme:



A termination reaction such as $\text{R}\cdot + \text{R}\cdot \rightarrow \text{R}-\text{R}$ has not been included, since the concentration of $\text{R}\cdot$ would be very low, and the reaction would require the mobility of polymer in a medium of high viscosity.

By assuming steady-state conditions for these radicals we obtain:

$$[\text{ROOH}] = [(k_3[\text{RH}] + k_4[\text{AH}])k_i[\text{RH}][\text{O}_2]/k_4k_5[\text{AH}]] (1 - \exp \{-k_5t\})$$

Therefore,

$$d[\text{ROOH}]/dt = [(k_3[\text{RH}] + k_4[\text{AH}])k_i[\text{RH}][\text{O}_2]/k_4[\text{AH}]] \times \exp \{-k_5t\} \quad (16)$$

$$d[\text{R}=\text{O}]/dt = [(k_3[\text{RH}] + k_4[\text{AH}])k_i[\text{RH}][\text{O}_2]/k_4[\text{AH}]] \times (1 - \exp \{-k_5t\}) \quad (17)$$

For the earlier stage, since time t is very small, eqs. (16) and (17) approximate the following equations:

$$d[\text{ROOH}]/dt = [(k_3[\text{RH}] + k_4[\text{AH}])k_i[\text{RH}][\text{O}_2]/k_4[\text{AH}]] \times (1 - k_5t) \quad (16')$$

$$d[\text{R}=\text{O}]/dt = [(k_3[\text{RN}] + k_4[\text{AH}])k_i[\text{RH}][\text{O}_2]/k_4[\text{AH}]]k_5t \quad (17')$$

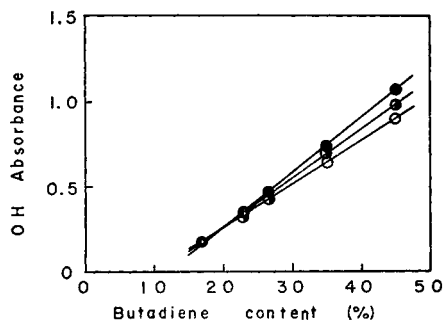
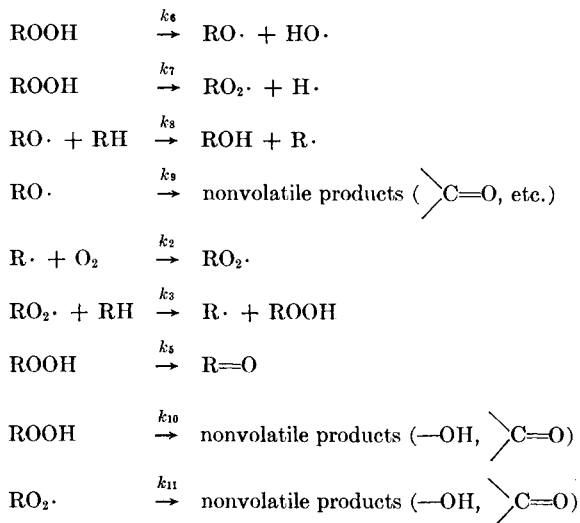


Fig. 12. Relation between hydroxyl absorbance and butadiene content in purified samples: (○) 70°C., oven; (◐) 80°C., oven; (●) 90°C., oven.

According to these equations, the formation of the oxidative products depend on k_i , k_3 , k_5 , $[RH]$, $[O_2]$, and $[AH]$ and carbonyl formation increases with heating time.

For the Part 2 reaction the following scheme is assumed:



By assuming the steady state, we obtained the following relation as the function of k and $[RH]$:

$$\begin{aligned}
 d[\text{OH}]/dt &= [\text{ROOH}]f_1(k, [\text{RH}]) \\
 d[\text{R=O}]/dt &= [\text{ROOH}]f_2(k, [\text{RH}])
 \end{aligned}$$

where f_1 and f_2 are functions.

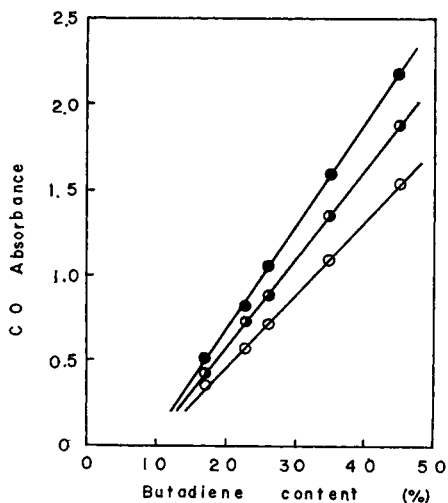


Fig. 13. Relation between carbonyl absorbance and butadiene content in purified samples: (○) 70°C., oven; (◐) 80°C., oven; (●) 90°C., oven.

As a result of these calculations, the following may be derived from the reaction scheme. For the later process the oxidative increase may be expressed by the formula $a - b \exp \{-ct\}$, where t is time, and a , b , and c are constants containing $[RH]$. Moreover, relative formations of hydroxyl and carbonyl are directly proportional to each other; this is in agreement with the experimental results.

Finally, a relation between oxide formation and the butadiene contents probably played an important part in the thermooxidative reaction. Figure 3 shows that the hydroxyl and carbonyl absorbances for aged samples were related to the butadiene contents of ABS resins. Figures 12 and 13 show that the higher the butadiene content, the easier the oxidation. Further, the higher the aging temperature, the greater the extent of oxidation.

We should like to express our gratitude to T. Takeda, K. Iino, and M. Akiyama, of the Electrical Communication Laboratory, Nippon Telegraph and Telephone Public Corp., for very helpful discussions.

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Received May 25, 1967

Revised July 31, 1967