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Factors Affecting the Stability of Cellulose Peroxides

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ABSTRACT

Factors affecting the stability of three kinds of cellulose peroxides prepared by reactions of aldehyde cellulose, carboxymethyl cellulose, and unmodified cellulose with hydrogen peroxide, Peroxides A, B, and C, respectively, were investigated. The relative stability of the peroxides was in the order Peroxide A > B > C, which was greatly improved by applying ethylenediaminetetraacetic acid as the chelating reagent for the metals in a very small amount in the sample. The sample kept under nitrogen retained stable activity of the peroxide longer than that under air atmosphere. Water in the sample seemed to participate in the decomposition of the peroxide to some extent. The functions of metals, water, and atmosphere on the decomposition of peroxide are discussed.

INTRODUCTION

In previous papers [1-3] cellulose derivatives having carbonyl and carboxyl groups were found to react with hydrogen peroxide (H_2O_2) to yield peroxides with structures of the α-hydroxyhydroperoxide and peracid types, respectively. These cellulose peroxides exhibited an ability to initiate thermal- and photo-graftings [1, 2, 4] of vinyl monomers. On the other hand, the preparation of cellulose peroxide was successfully performed by treating unmodified cellulose with H_2O_2 directly [5]. However, the peroxide groups on the sample were considerably unstable and almost all of them ran out within 10 d under air atmosphere at ambient temperature. In an attempt to achieve practical application of the peroxide materials, it is important to consider ways to retain stable activity as long as possible.

The purpose of this study is to reveal various factors affecting the decomposition of the peroxides on cellulose samples and to find the way improving their stabilities.

EXPERIMENTAL

Three cellulose peroxide samples were prepared as follows. Aldehyde cellulose was obtained by oxidation of dissolved pulp from softwood (NDP) with periodic acid. It was reacted with 35% aqueous solution of H_2O_2 at 30°C for 3 h to prepare Peroxide A [1]. Fibrous carboxymethyl cellulose (degree of substitution, 0.15), prepared by the reaction of NDP with monochloroacetic acid, was treated with a 35% aqueous solution of H_2O_2 containing sulfuric acid to yield Peroxide B [3]. Peroxide C [5] was directly prepared from NDP, on which a known volume of 1.75% aqueous solution of H_2O_2 had been atomized, by storing it at room temperature for 3 d.

The reacted products were washed with ice water, and then the cellulose peroxide samples were filtered to obtain wet samples containing about 80% water. The water in the wet samples was replaced by methanol, followed by drying under reduced pressure to prepare dry samples.

A known volume of water-methanol mixture dissolved in ethylenediaminetetraacetic acid (EDTA) was atomized on the cellulose peroxide, which was then dried under reduced pressure to obtain an EDTA-added sample. The quantity of EDTA added was taken as the percentage to the absolute sample. The amount of the peroxide group was determined iodometrically.

RESULTS

Figure 1 shows the change in the amount of peroxide remaining in the substrate being stored under an air atmosphere at 20°C. The stability of dry samples was in the order Peroxide A > B > C. The stability of wet samples was of the same order as the dry samples, although the level was very low compared to the dry samples. Each peroxide sample was characterized by a sharp decomposing reaction of the peroxide group after a certain induction period. As clearly seen in Fig. 2, the induction period was greatly reduced at 30°C,

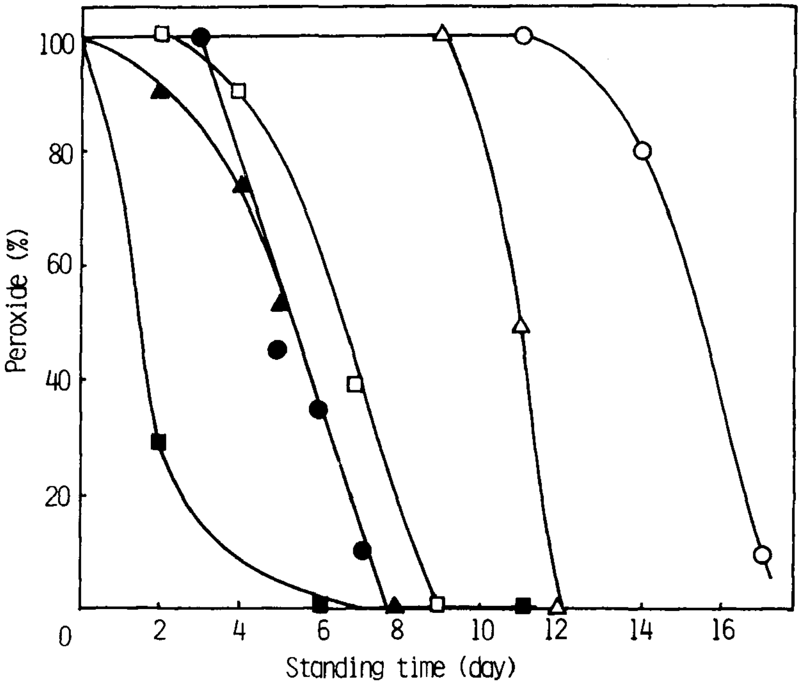


FIG. 1. Stability of cellulose peroxides at 20°C under air atmosphere. Initial amount of peroxide Samples A (○, ●), B (△, ▲), and C (□, ■) are 28.3, 26.8, and 25.0 meq/100 g cellulose. (○, △, □) Dry sample. (●, ▲, ■) Wet sample.

indicating a large dependence of the decomposing reaction on temperature.

It is generally known that the decomposition of peroxides is markedly activated by metal ions [6]. Cellulose samples, especially wood pulp [7, 8], are believed to contain a very small amount of metals by nature. Accordingly, the decomposition of cellulose peroxide is expected to be suppressed by trapping the metals with a chelating reagent. Figure 3 shows the effect of EDTA as a chelating reagent. Stability of the peroxide sample was highly improved with EDTA. However, EDTA employed beyond a certain quantity tended to reduce the stability of the peroxide gradually.

Figure 4 shows the effect of atmosphere on the stability of cellulose peroxides. The decomposing reaction of peroxide was found to be milder for samples stored under nitrogen atmosphere than for those under air. A negligible effect of atmosphere was recorded for the EDTA-added sample.

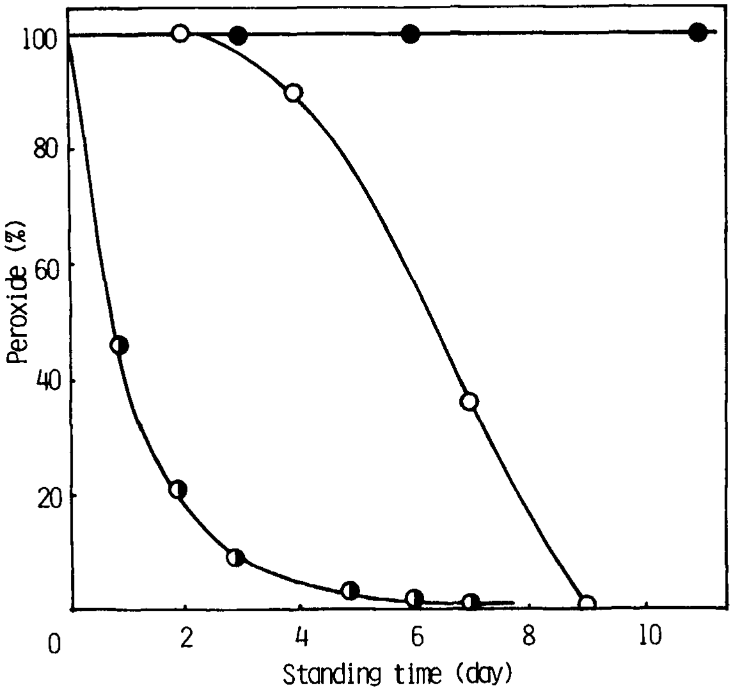


FIG. 2. Effect of temperature on stability of dry peroxide Sample C under air atmosphere. Initial amount of peroxide; 25.0 meq/100 g cellulose. (•) 5°C, (○) 20°C, (◑) 30°C.

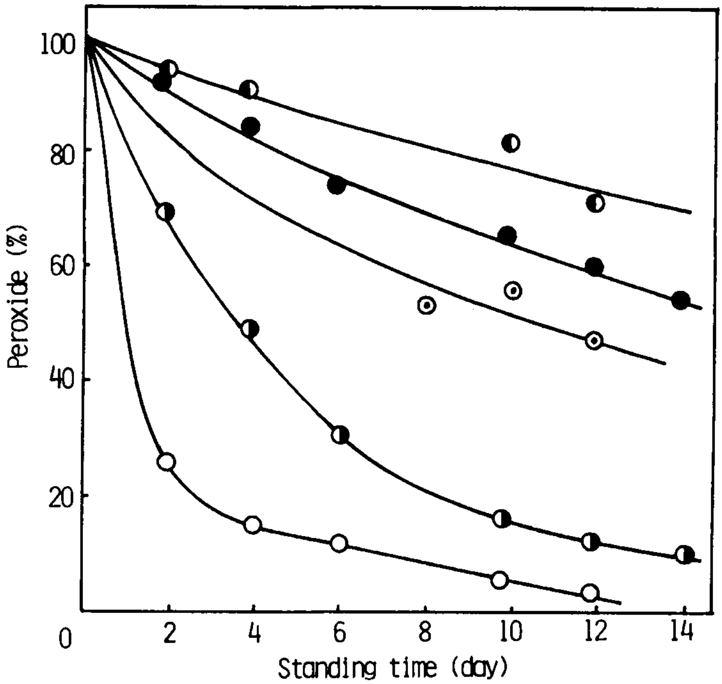


FIG. 3. Effect of EDTA on stability of dry peroxide Sample A at 30°C under air atmosphere. Initial amount of peroxide; 23.2 meq/100 g cellulose. Concentration of EDTA (%): (○) 0, (◑) 0.01, (◐) 0.1, (●) 0.5, (⊙) 5.0.

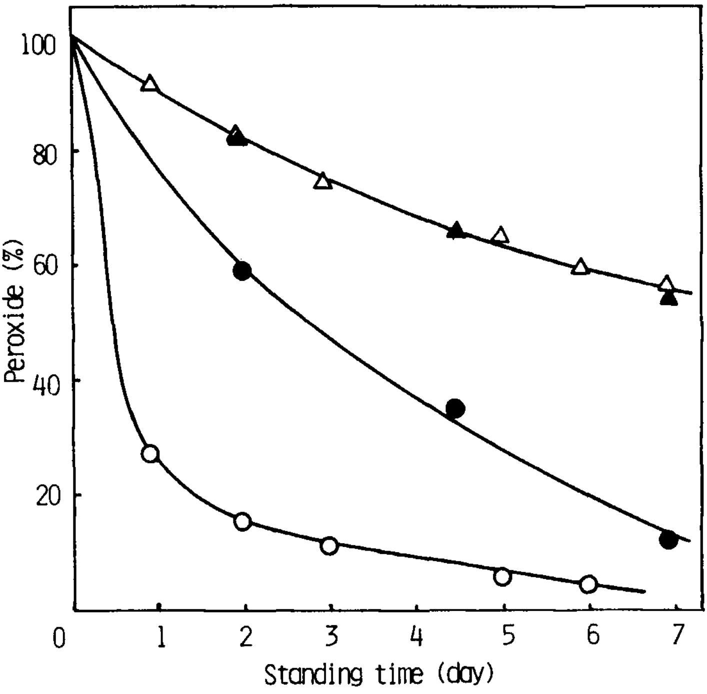


FIG. 4. Effect of atmosphere on stability of dry peroxide Sample A at 30° C. Initial amount of peroxide; 14.0 meq/100 g cellulose. Peroxide sample without EDTA: (○) under air, (●) under nitrogen. EDTA (0.5%)-added peroxide sample: (△) under air, (▲) under nitrogen.

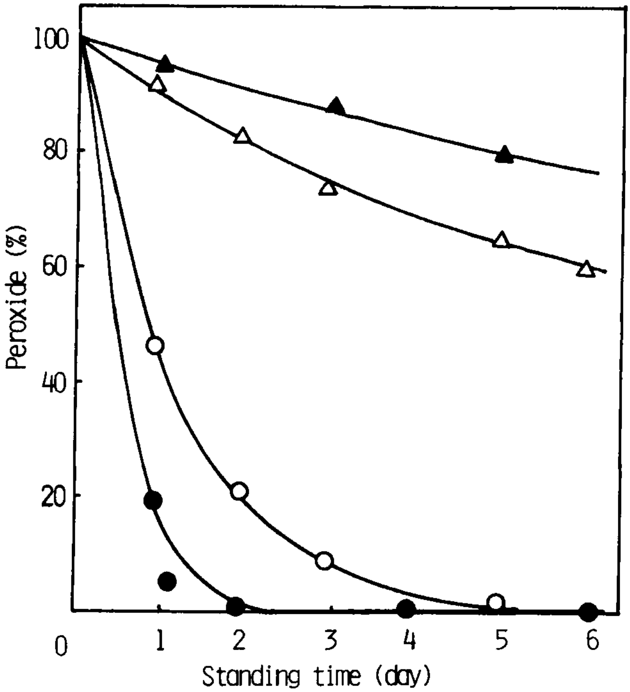


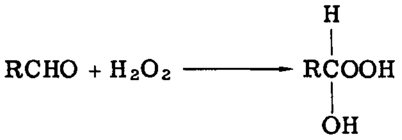
FIG. 5. Effect of EDTA on stability of peroxide Sample A at 30°C under air atmosphere. Initial amount of peroxide; 25.1 meq/100 g cellulose. Peroxide sample without EDTA: (○) dry sample, (●) wet sample. EDTA (0.5%)-added peroxide sample: (△) dry sample, (▲) wet sample.

Water in the sample is shown to reduce the stability of peroxide in Fig. 1. EDTA was applied to the wet samples in Fig. 5. As expected, the stability of the wet samples was remarkably improved by EDTA.

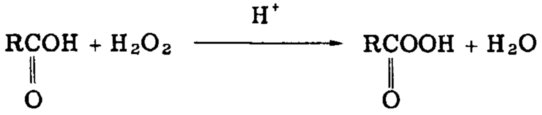
Factors such as metals, atmosphere, and water significantly affected the stability of the three peroxide samples.

DISCUSSION

Peroxides A [1] and B [3] may be formed according to Eqs. (1) and (2) to give main structures of the α-hydroxyhydroperoxide and peracid types, respectively:



$$\mathrm{RCHO + H_2O_2 \longrightarrow R\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle OH}{|}}{C}}OOH} \qquad (1)$$

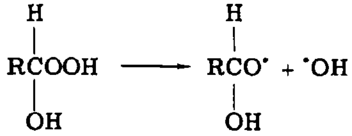


$$\mathrm{R\underset{\underset{\displaystyle O}{\|}}{C}OH + H_2O_2 \xrightarrow{H^+} R\underset{\underset{\displaystyle O}{\|}}{C}OOH + H_2O} \qquad (2)$$

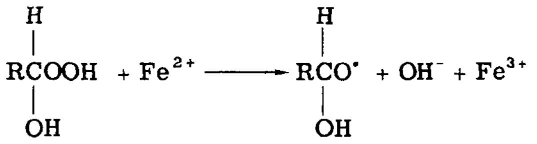
where RCHO and $\mathrm{R\underset{\underset{\displaystyle O}{\|}}{C}OH}$ denote aldehyde cellulose and carboxymethyl cellulose, respectively.

Peroxide C [5] can be obtained by oxidizing cellulose with H_2O_2 to yield oxidized groups, such as a ketone group, on the substrate. This is followed by peroxidizing with H_2O_2, resulting in peroxide groups. Thus the structure of Peroxide C is believed to resemble closely that of Peroxide A.

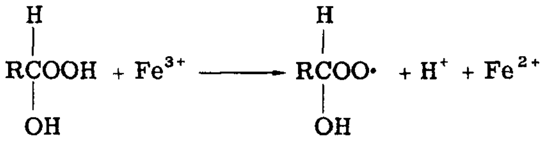
The stabilities of the three cellulose peroxides appear quite different as shown in Fig. 1. The stability was lowest for Peroxide C, although the same level of stability was expected for Peroxide A because it has the same structure. The reason for this is not clear. However, the oxidized state of each sample should be affected by the stability of the peroxide groups. Further studies on the structure of Peroxide C and its characteristics will be required.



$$\mathrm{R\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle OH}{|}}{C}}OOH \longrightarrow R\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle OH}{|}}{C}}O^{\bullet} + {}^{\bullet}OH} \qquad (3)$$



$$\mathrm{R\overset{H}{\underset{OH}{C}}OOH} + \mathrm{Fe}^{2+} \longrightarrow \mathrm{R\overset{H}{\underset{OH}{C}}O^{\bullet}} + \mathrm{OH}^{-} + \mathrm{Fe}^{3+} \tag{4}$$



$$\mathrm{R\overset{H}{\underset{OH}{C}}OOH} + \mathrm{Fe}^{3+} \longrightarrow \mathrm{R\overset{H}{\underset{OH}{C}}OO\cdot} + \mathrm{H}^{+} + \mathrm{Fe}^{2+} \tag{5}$$

$$\mathrm{Fe}^{2+} + \mathrm{O}_2 \longrightarrow \mathrm{Fe}^{3+} + \mathrm{O}_2^{-} \tag{6}$$

The decomposition of Peroxide A seems to proceed essentially according to Eq. (3). Considering iron as the metal in the cellulose sample, for example, ferrous and ferric ions may participate in the decomposition of peroxide by means of a redox reaction according to Eqs. (4) and (5), respectively. Enhanced thermal decomposition [1, 4] of Peroxides A and B has been observed by applying iron ions. If EDTA can mask the iron ions through chelation, the decomposition of peroxide group is sure to be suppressed, resulting in improved stability.

On the other hand, the cellulose peroxides were stabilized somewhat under nitrogen atmosphere (Fig. 4). It is plausible that ferrous ion is oxidized to ferric ion according to Eq. (6) in the presence of oxygen. The resultant ferric ion promotes the decomposition of peroxide according to Eq. (5). Because Eq. (6) may not take place under a nitrogen atmosphere, the stability of the peroxide is increased. No effect of oxygen on peroxide stability was observed for the EDTA-added sample (Fig. 4). This fact can be ascribed to the EDTA function.

From previous papers [1, 4], Peroxides A and B are known to liberate H_2O_2 from the substrate due to the reverse reactions of Eqs. (1) and (2) by contact with water. In the wet sample, the peroxide group and H_2O_2 keep a certain equilibrium. The liberated H_2O_2 may naturally be attacked by iron ions, resulting in the accelerated decomposition of peroxide in the wet sample (Figs. 1 and 5).

From the above results the cellulose peroxides were proven to be affected by such factors as metals, water, temperature, and atmosphere. It can be concluded, therefore, that a high level of improvement in the stability of cellulose peroxide can be achieved by a combination of these factors.

REFERENCES

[1] Y. Ogiwara, T. Umasaka, and H. Kubota, J. Appl. Polym. Sci., 23, 837 (1979).
[2] H. Kubota and Y. Ogiwara, Ibid., 25, 683 (1980).
[3] H. Kubota and Y. Ogiwara, Ibid., 22, 3363 (1978).
[4] H. Kubota and Y. Ogiwara, Ibid., 23, 241 (1979).
[5] Y. Ogiwara and H. Kubota, Cellulose Chem. Technol., To Be Published.
[6] D. Swern (ed.), Organic Peroxides, Vol. II, Wiley, New York, 1970, p. 153.
[7] E. Otto, M. Spurlin, and M. W. Grafflin (eds.), Cellulose and Cellulose Derivatives, Part III, Interscience, New York, 1954, p. 1364.
[8] S. A. Rydholm, Pulping Processes, Wiley-Interscience, New York, 1965, p. 1115.

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