Reaction of Sodium Perborate with a Chlorinated Cyclic Hindered Amine (N-chloro-4-hydroxy-2,2,6,6-tetramethylpiperidine) II. Activating Effects and Related Characteristics in Practical Fabric Bleaching

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ABSTRACT: A synergetic bleaching activation phenomenon of the chlorinated cyclic hindered amine, N-chloro-4-hydroxy-2,2,6,6-tetramethylpiperidine (TMP–Cl) on sodium perborate (PB) was examined under some practically applicable bleaching procedures. By combining TMP–Cl with PB, the bleaching effect toward black tea, fruit juices and other stains was enhanced synergetically, achieving an efficiency similar to that of the well-known tetraacetylethylenediamine/PB system. However, behavior observed in the TMP–Cl/PB system, such as high bleaching efficiency in an alkaline range, superior durability for repeated bleaching, less discoloration of cloth that contains reactive dyes and no influence on the activity of an enzyme, was favorable for a bleaching component of heavy-duty detergents.

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KEY WORDS: Activator, detergent, discoloration, dye, enzyme activity, oxidative bleaching agent, stain.

Hydrogen peroxide adducts such as sodium perborate (PB) and sodium percarbonate (PC) have been widely used as the bleaching component of fabric bleach compositions and heavy-duty detergents for both home and institutional use. However, the bleaching efficiency of these compounds was not satisfactory, especially under low-temperature conditions. Since the 1970s, public trends toward energy saving have stimulated studies to improve the bleaching efficiency of hydrogen peroxide adducts even at low temperature.

Various types of bleaching activators, such a tetraacetylethylenediamine (TAED), tetraacetylglycol uril (TAGU), pentaacetylglucose (PAG) and alkanoyloxybenzenesulfonate (AOBS) have been reported in many patents (1–3) and literature sources (4,5).

The bleaching activation efficiency of these compounds has been considered to be derived from the formation of perfatty acid (4,5), which has a high bleaching potential, even at low temperature. In addition to these, many other activating methods, such as the radical decomposition of the hydrogen peroxide by heavy metal ions (6,7) and the generation of singlet oxygen by light-sensitizing dyes (8), have been reported.

Among these methods, the application of chemically generated singlet oxygen has hardly been investigated yet. As conventional methods for chemical generation of singlet oxygen, the HOO^-/ClO^- system (9), decomposition of potassium perchromate (10), decomposition of superoxide ion (11) and base-induced decomposition of peroxyacetylnitrate (12) are well known. The HOO^-/ClO^- systems, composed with commercially available materials such as PC or PB/NaClO and PC or PB/dichloroisocyanurate, cannot develop practically acceptable bleaching efficiency because such sources of ClO^- have a relatively large hydrolysis constant K_h (13), and consequently, they react with HOO^- at too high a rate to keep an adequate steady-state concentration of singlet oxygen. On the other hand, we have reported that N-chloropiperidine and N-chloro-*t*-butylamine derivatives with a small K_h of around 10^{-7}–10^{-6} showed high activation efficiency (14). In this paper, the characteristics of N-chloro-4-hydroxy-2,2,6,6-tetramethylpiperidine (TMP–Cl) as a bleaching activator for perborate will be examined under conditions simulating practical use.

EXPERIMENTAL PROCEDURES

Materials. PB with an available oxygen content of 15.3 wt% was a commercial product obtained from Mitsubishi Gas Chemical Co., Ltd. (Tokyo, Japan). TAED was a commercial product obtained from Warwick International, Ltd. (London, England). These were used without purification.

TMP–Cl was synthesized according to the method of Rigo *et al.* (15). An aqueous solution of NaClO (0.05M) was added to an aqueous solution (0.05M) of 4-hydroxy-2,2,6,6-tetramethylpiperidine (TMP–H) at about 0°C. The solution was stirred for one hour, followed by extraction with *n*-hexane. Evaporation afforded colorless needles of TMP–Cl (m.p. 86–87°C, λ_{max} = 240–250 nm).

A granular detergent, utilized for the detergency test, was a commercial product (Lion Corp., Tokyo, Japan). The protease enzyme (Subinase) was purchased from NOVO Industries Co. (Tokyo, Japan).

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Test cloths for the bleaching test were prepared by dipping cotton cloth in black tea extract, red wine, red gooseberry juice and black gooseberry syrup for one hour at 60°C, followed by squeezing, rinsing with tap water (hardness: approx. 3°DH) and drying in air.

The test cloths for the evaluation of dye discoloration were prepared by treating cotton cloths with a reactive dye, Reactive Red-21 (Brilliant Red BB; Mitsubishi Chemical Co., Ltd., Tokyo, Japan) according to the conventional method.

The test cloths for the detergency evaluation were prepared by treating cotton cloth with artificial soil, which is composed of oleic acid, triolein, cholesterol oleate, casein and carbon black, according to the conventional method.

Evaluation of bleaching efficiency and dye discoloration. PB and bleaching activator were dissolved in 200 mL water, of which the hardness and temperature were previously regulated. Ten test cloths, 5 × 5 cm, were dipped in the solution for a given period, rinsed with tap water and dried in air. The degree of reflection of the stained cloths before and after the bleaching treatment was measured by a colorimeter (Japan Electric Color Industry Co., Ltd., Tokyo, Japan). The percent bleaching efficiency was calculated by the Equation 1:

$$\text{bleaching efficiency (\%)} = (R_w - R_s)/(R_o - R_s) \times 100 \qquad [1]$$

where R_w = degree of reflection of stained cloth after bleaching treatment; R_s = degree of reflection of stained cloth before bleaching treatment; and R_o = degree of reflection of cloth before stain treatment.

The bleaching efficiency (%) expressed in Equation 1 merely describes the apparent restoration of the lightness by bleaching. We used the bleaching efficiency (%) calculated by Equation 1 as one of the indexes of bleaching efficiency.

The accuracy of the bleaching efficiency (%) for all bleaching tests was better than ±2.5% as represented by the standard deviation. When these test cloths were treated with a detergent solution without a bleaching agent, the bleaching efficiencies (%) obtained were −19% for black tea, 25% for red wine, 8% for red currant and 21% for black current, respectively (40°C, 15°DH, 30 min).

The test for dye discoloration was undertaken as follows. A powder mixture of 0.15 g of PB and 0.15 g of bleaching activator was placed on a cloth colored with Red-21, followed by spraying with a small amount of water. After standing for 30 min, the cloth was rinsed with tap water and air-dried. The degree of the speckled discoloration was evaluated by eye inspection. Although this procedure appears to be very severe, the evaluation was made on the assumption of unusual misuse.

Evaluation of the influence on the activity of the enzyme by the PB/TMP–Cl system. Granular detergent (0.2 g) containing 0.3 wt% protease-type enzyme, 6 wt% PB and 2 wt% TMP–Cl was dissolved in 150 mL of 3°DH water, and 10 artificially soiled cloths, 5 × 5 cm, were dipped in the solution at 40°C for 1 h. The solution was then diluted five times with 3°DH water and washed in a Terg-o-tometer (120 rpm) at 25°C for 10 min, subsequently rinsed and dried. Detergency was calculated from the reflection of the soiled cloths before and after washing by using Kubelka-Munk's equation. The remaining enzyme activity was estimated from the detergency level.

RESULTS AND DISCUSSION

Bleaching activation efficiency of TMP–Cl. Figure 1 shows the change in bleaching efficiency toward black tea stains as a function of PB concentration. For all systems, the bleaching efficiency was abruptly increased in the low concentration range; whereas, it was gradually increased in the high concentration range. At a ratio of [PB]/[activator] = 84:16 (mole/mole), a pronounced high bleaching efficiency was observed in both the PB/TMP–Cl and PB/TAED systems through the overall concentration range. At a low concentration, TMP–Cl and TAED showed almost the same activation efficiency, but at a higher concentration, TMP–Cl showed a higher activation efficiency.

The relation between temperature of the bleaching bath and bleaching efficiency is shown in Figure 2, which demonstrates a rapid increase in bleaching efficiency with an increase in temperature for all systems.

Figure 3 shows the relationship between the pH of the bleaching bath and bleaching efficiency. In contrast with the PB/TAED system, which has a high bleaching efficiency at low pH, the PB/TMP–Cl system shows a high bleaching efficiency at high pH. This is reasonable if one considers that peracetic acid, which is claimed to be formed in the bleaching bath of the PB/TAED system, contributes to the bleaching,

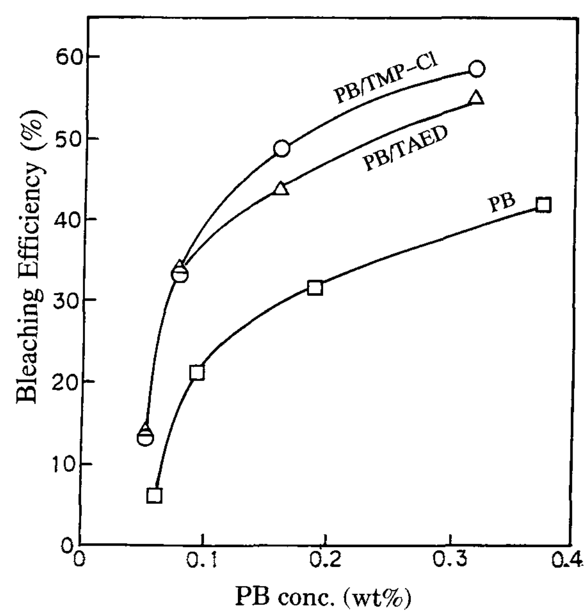

FIG. 1. Bleaching efficiency of sodium perborate (PB)/activator systems toward tea-stained fabric as a function of PB concentration. [PB]/[activator] = 84/16(mole/mole), 15°DH, 40°C, 30 min. TMP–Cl, N-chloro-4-hydroxy-2,2,6,6-tetramethylpiperidine; TAED, tetraacetylethylenediamine.

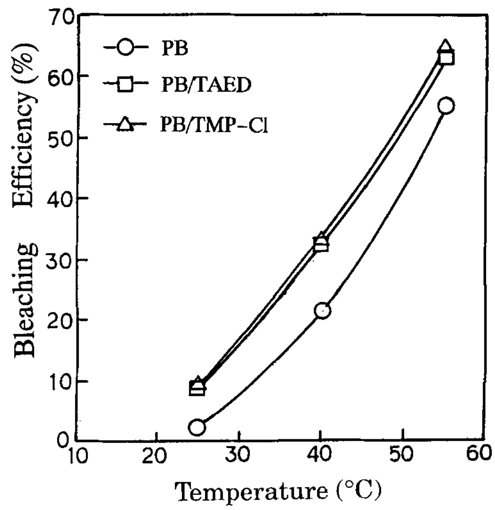

FIG. 2. Bleaching efficiency of PB/activator systems toward tea-stained fabric as a function of temperature. PB = 0.0788 wt%, [PB]/[activator] = 84/16 (mole/mole), 15°DH, 30 min. See Figure 1 for abbreviations.

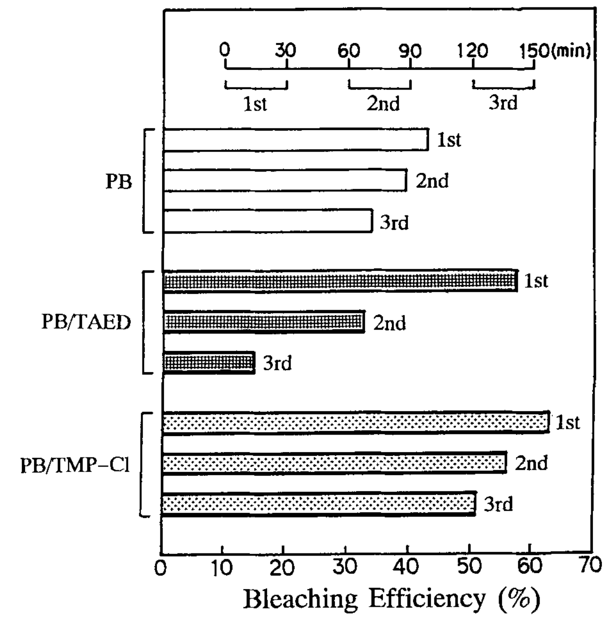

FIG. 4. Variation of bleaching efficiency of PB/activator systems on repeated bleaching. PB = 0.315 wt%, [PB]/[activator] = 84/16 (mole/mole), 15°DH, 40°C, tea-stain. See Figure 1 for abbreviations.

because peracetic acid itself shows maximum bleaching efficiency near pH = 8 (4). On the other hand, the PB/TMP–Cl system can be accounted for by the action mechanism [discussed in the preceding paper (16)]. At any rate, when one considers a method of adding PB and an activator as components of a heavy-duty detergent, TMP–Cl, with a high activation efficiency at high pH, is assumed to be an appropriate bleaching activator for compounding into heavy-duty detergent, because most heavy-duty detergents are formulated to create a pH of 10–11 in use.

Figure 4 compares the durability of bleaching on repeated use of cloth stained by black tea in the same bleaching bath. Although the bleaching efficiency decreased significantly on repetition for the PB/TAED system, the decrease in bleaching efficiency was small in the PB/TMP–Cl system and the PB system. In particular, the PB/TMP–Cl system maintained a high bleaching efficiency level, even after three repetitions of bleaching. This superior durability of the PB/TMP–Cl system on repeated bleaching can be accounted for by the action mechanism [discussed in the preceding paper (16)].

Figure 5 shows the effect of each bleaching system for various stains except for black tea stain. For any stains, the PB/TMP–Cl system showed a bleaching efficiency similar to that in the PB/TAED system and a clear bleaching activation efficiency toward PB.

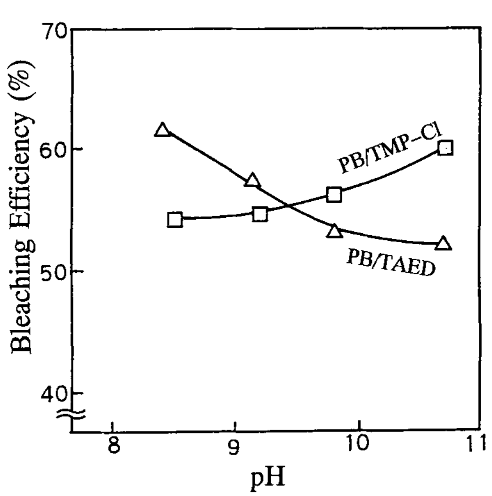

FIG. 3. Bleaching efficiency of PB/activator systems toward tea-stained fabric as a function of pH. PB = 0.315 wt%, [PB]/[activator] = 84/16 (mole/mole), 15°DH, 40°C, 30 min. See Figure 1 for abbreviations.

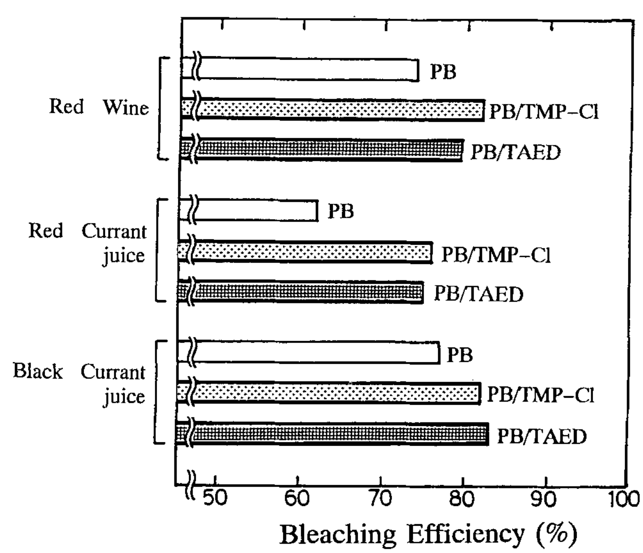

FIG. 5. Bleaching efficiency of PB/activator systems for various stains. PB = 0.0788 wt%, [PB]/[activator] = 84/16 (mole/mole), 15°DH, 40°C, 30 min. See Figure 1 for abbreviations.

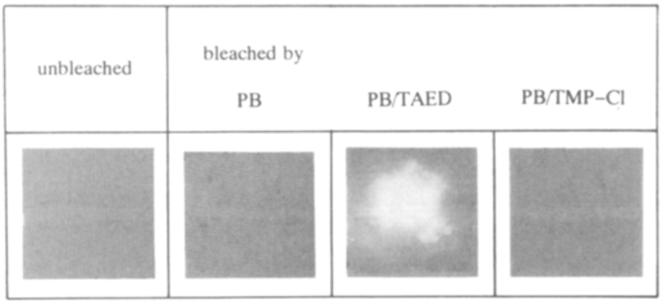

FIG. 6. Decolorizing of the colored cloth by PB/activator mixtures. See Figure 1 for abbreviations. Magnification: ×0.7.

Decolorizing effect of activator for colored fabrics. Although the PB/TMP–Cl system has a high bleaching efficiency toward various stains, it was found to show mild characteristics toward some kinds of reactive dyes. Because the distribution of fabrics colored by reactive dyes has increased in recent years, examination of the influence of bleaching systems toward fabrics colored by reactive dyes is important. Figure 6 shows the decolorizing effect of various bleaching reagent systems toward cloth colored by Red-21. Although the PB/TAED system induced drastic decolorization, the PB/TMP–Cl system showed almost no effect, as did the PB system.

Influence of TMP–Cl on enzyme activity in detergent solution. In general, active chlorine in water deactivates the enzymes that are frequently formulated in heavy-duty detergents. Because TMP–Cl has a chlorine atom in its molecule, influence on the activity of protease in detergent solution was examined. Table 1 shows the effect of PB/TMP–Cl system on the detergency of artificially soiled cloth. Based on the results, the detergency enhanced by protease was not suppressed by the PB/TMP–Cl system, we conclude that this system does not inhibit the protease activity in detergent solution.

TABLE 1
Influence of the PB/TMP–Cl System on the Enzyme Activity of Detergent Solution

System	Detergency (%)
Detergent	90
Detergent + Protease	96
Detergent + Protease + PB/TMP–Cl[a]	96
Detergent + PB/TMP–Cl	90
Detergent formulation:	
Sodium alkyl benzenesulfonate (C_{10-14})	10 wt%
Sodium alpha-olefinsulfonate (C_{14-18})	10 wt%
Sodium alkylsulfate (C_{10-16})	2 wt%
Zeolite	16 wt%
Sodium silicate	10 wt%
Sodium carbonate	10 wt%
Thinopearl CBS-X (fluorescent brightener)[b]	0.2 wt%
Water	5 wt%
Sodium sulfate	Balance

[a]PB/TMP–Cl, sodium perborate/N-chloro-4-hydroxy-2,2,6,6-tetramethylpiperidine.
[b]From Ciba-Geigy AG (Basel, Switzerland).

This research has shown that: (i) The TMP–Cl had a pronounced bleaching activation efficiency, comparable to that of the well-known TAED; and (ii) The TMP–Cl had several unique characteristics as an activator for heavy-duty detergents, such as high bleaching efficiency in an alkaline range, superior durability for repeated bleaching, smaller discoloration of cloth containing reactive dyes and no influence on the activity of the enzyme.

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