Fabric Bleaching with Sodium Perborate

L. T. MURRAY, Research and Development Center,
Colgate-Palmolive Company, Piscataway, New Jersey 08854

Abstract

Presently two classes of fabric bleaching agents, the chlorine and oxygen types, are employed in home laundering. Although these two classes of bleaches are employed, there is a vast difference in their effectiveness. The chlorine bleaches function well under most time and temperature conditions practiced in fabric laundering in the United States, but equivalent effectiveness with the oxygen type can only be obtained under longer time or higher temperature use conditions.

This paper represents a review of the relative performance and cost of the two classes and concentrates on the considerable research activity of the last 20 years, directed toward finding routes to increased bleaching effectiveness with sodium perborate. The chemistry of these approaches, consisting primarily of the use of the so-called organic activators and metal ion catalyst systems, is discussed along with a discussion of effectiveness, cost, and potential utility.

Introduction

THE PRESENT DAY BUILT LAUNDRY DETERGENTS may not completely clean fabrics from all types of stains and soils. Residual food stains, soils of sebaceous origin, such as fatty acids, glycerides, and oxidation products thereof, and particulate soils are among the more common soils which may not be completely removed by detergent washing (1,2).

Various additives, such as whiteners and brighteners or bleaching agents, have been incorporated into, or are used in conjunction with, detergent products. In the first case the function is to mask residual soil and brighten fabrics, and in the second case, to remove or decolorize soil via oxidative reaction.

The classes of oxidizing agents which have successfully been used for this purpose have been limited by their effectiveness in such an operation, their cost, and their ease and safety in use, both to the user and the fabric. Therefore only two classes of compounds have found some application, namely, the chlorine and oxygen types.

The liquid chlorine type, that is, aqueous hypochlorite solution, has gained most acceptance in the United States because it offers an inexpensive, highly effective agent when used in low concentrations of the order of 100 to 200 ppm. Although there are drawbacks to the use of the chlorine type, such as the possibility of overuse or misuse which may result in fabric damage or the limitation on use with colored fabrics and types of fabrics, the advantages of cleaning far outweigh these manageable disadvantages. Indeed, hypochlorite solution is used in many laboratories as a standard for effective bleaching. The fact that it has withstood the test of time in spite of the challenge by N-chloro bleaches, which offer chlorine in a solid, captive form for ease of handling, use, and minimization of odor, speaks well for hypochlorite effectiveness.

TABLE I

Comparison of Bleaches at 120F
Anionic Detergent
Oxidants at Equimolar Levels of Order of 10^{-3} M

Soil	Final Values		
	Rd (detergent)	Rd (detergent + 'O')	Rd (detergent + 'Cl')
Grape	58.7	61.2	83.7
Wine	82.9	83.5	89.0
Sulfa dye	......	20.9	62.0
Coffee/Tea	......	73.0	87.0

The oxygen type of bleaches, as represented by compounds such as sodium perborate or potassium monopersulfate, have had less impact on domestic laundering. While the oxygen bleaches are regarded as safe bleaches, that is, not damaging the fabric as can the chlorine type, they are not effective bleaching agents. This can be seen from an inspection of the data in Table I. These data were collected in Terg-o-Tometer washing tests on swatches stained with the soils mentioned in the table. The tests were conducted for 10 or 15 min at equimolar concentration of oxidants, equivalent to 200 ppm available chlorine and 45 ppm active oxygen. In simple wash tests, with various soils, the differences can be noted. The magnitude of difference may be dependent on the sensitivity of the particular soil to each oxidizer, but the order of the effect is quite obvious.

Although the United States market has progressed along the chlorine route, the case is different in Europe, where laundering technology has been built upon presoaking and/or laundering for longer periods of time with hotter temperatures. A typical European situation might entail use of temperatures approaching the boil for times up to 60 min whereas temperatures not in excess of 120–140F for 10–20 min are more common in the United States. Under such European conditions of time and temperature, sodium perborate behaves as an effective, yet safe bleach toward fabrics. Therefore it has evolved as the major fabric bleach in Europe and is commonly a significant component of built laundry detergents.

Perborate does perform in poorer fashion compared with chlorine bleaches under the United States conditions, but it offers the advantage of a mild, easily handled, odor-free, detergent-formulatable bleaching agent. Also it offers a cost advantage as a bleach compared with solid N-chloro compounds.

Actually, sodium perborate is a compound which breaks into hydrogen peroxide and sodium metaborate in solution (3). This is to be distinguished from compounds, such as potassium monopersulfate or peroxydisulfate which are true inorganic peroxides, where the peroxide linkage is to sulfur atom. The following is a summary of the pertinent peroxide chemistry:

$$NaBO_3 \cdot 4\,H_2O = NaBO_2 \cdot H_2O_2 \cdot 3\,H_2O = H_2O_2 \text{ (AQUEOUS SOLUTION)}$$

$$pKa\ H_2O_2 \cong 11.5$$

$$H_2O_2 - \text{AQUEOUS SOLUTION}$$

$$(1)\ HO_2^- + H_2O + 2e^- \longrightarrow 3\,OH^- \text{ (OXIDATIVE ACTION - BLEACHING)}$$

$$(2)\ HO_2^- + OH^- - 2e^- \longrightarrow O_2\uparrow + H_2O \text{ (REDUCTIVE ACTION - DECOMPOSITION)}$$

Considerable research activity has been directed in the last 20 years toward developing methods which will either increase the bleaching of perborate within the framework of higher washing temperatures or, by avoidance of the thermal route, increase the medium temperature bleaching effect within the framework of shorter time and lower concentration conditions. The major approaches have centered on the use of inorganic catalysts and the so-called organic activators.

Discussion

Inorganic Catalysis

It has been well established that the mild oxidative power of hydrogen peroxide may be increased by the use of certain metallic catalysts. This effect was first observed by Fenton with his hydrogen peroxide-ferrous ion system (4). This redox system, as exemplified below, is believed to function via one electron transfer step with the generation of a hydroxyl free radical.

$$Fe^{++} + H_2O_2 \longrightarrow Fe^{+++} + OH^- + \cdot OH$$

This system proceeds through the formation of metal peroxide prior to radical formation.

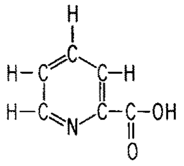
There are many oxidation applications. The ferrous-ferric system and other redox systems, such as the cuprous (the +1 oxidation state) — cupric (the +2 oxidation state) system, are normally used with hydrogen peroxide under acid conditions. As solvent acidity decreases, the efficiency of the oxidation reaction is reduced and more catalytic decomposition of peroxide occurs. The latter is a drawback to the proposed application to bleaching. It is well known that conventional laundering treatments are carried out in alkaline media with pH values of 9 to 10. A few simple experiments are enough to convince observers that metal ion catalysis of peroxide in alkaline bleach baths leads primarily to peroxide decomposition and to no substantial bleaching acceleration. However, with such an economically attractive system, namely, the use of metal ions in truly catalytic quantities, research has continued in this area.

The next logical step, the incorporation of chelating agents into the system, has met with more success. It is predicated on the assumption that, in the previous system, with no chelating agent present, decomposition of peroxide takes place throughout the wash solution rather than in the proximity of the soil where it may have an effect. With chelating agents it is proposed that their function is to complex the free metal ion catalyst in solution. This approach avoids wasted catalytic decomposition of peroxide in solution by the free metal ion or hydroxides and oxides thereof. The only free metal ions are those that have been adsorbed onto the fabric in the wash. Any action on peroxide is forced to occur where the effect is needed, on the soiled cloth. In theory, then, a proper balance of chelating agent/metal ion is required so as to give a significant enough rate of bleaching in the proximity of the soil in the laundering time allowed, with a minimum of wasted decomposition in solution.

The development of such systems is not based solely upon the combination of any metal ion with any chelating agent. More properly, the chelating agent must not be so powerful that it selectively ties up all free metal ion and does not allow deposition of some free metal ion on the cloth. Conversely, the chelate should not be so weak that it allows too much metal ion to be adsorbed onto the cloth or some of the metal ion to remain free in solution. For this type of approach to be successful, the above factors along with the effect of the specific metal ion with peroxide must be taken into account.

A number of such metal ion-chelate systems have been claimed in the patent literature, for increased bleaching effect at moderate and high temperatures. Some of the successful systems developed (5,6) are summarized as follows:

Co^{+2} 2 PYRIDINECARBOXYLIC ACID



Cu^{+2} NITRILOTRIACETIC ACID

$N(CH_2COOH)_3$

A typical set of data for the cobalt-pyridine-2-carboxylic acid system, a moderate temperature system, and the copper-NTA type of system, a high-temperature system, are reproduced from the literature in Table II.

Although this approach has been demonstrated with model soil systems and would offer an economically feasible activator route, owing to the low concentration of metal ion-chelate required, this effect is variable when transferred to ordinary laundering conditions. When it is considered that a critical balance of the two ingredients needs to be maintained and this must be accomplished in a system beset with problems, such as pH variation, variation in soil load and type, potential incorporation of other catalytically active metal ions via the water or soil (all potential complicators to the preferred ratio of components), it is not surprising that these systems have not found practical application.

Organic Activators

The second approach to activation is the use of the so-called organic activators. It has long been known that organic peroxides and, more particularly, organic peroxyacids are effective oxidizing agents (7). However their direct use in fabric-bleach applications has been limited by their cost, difficulty of preparation, inherent chemical instability, and finally prob-

TABLE II

Cobalt Sulfate-(Pyridine-2-Carboxylic Acid) System
3×10^{-5} M in Co^{+2}
2.5×10^{-4} M in chelate

$NaBO_3 \cdot 4H_2O$ (g/liter)	Increase in Reflectance (ΔR)		
	Without catalyst 60C	Without catalyst 100C	Co^{+2}-chelate 60C
1.25	1	3	9.3
5.00	....	....	16.3
10.00	6.1	11	16.9

Copper Sulfate-NTA System
5×10^{-5} M in Cu^{+2} and NTA

$NaBO_3 \cdot 4H_2O$ (g/liter)	% Bleaching Efficiency-100C	
	No chelate	Chelate
0.5	39	60
1.25	51	73

lems associated with the stability of the formulated product.

Therefore a more logical approach has been the attempted in-situ formation of such peroxyacids in the presence of water, laundering agent, and fabric, that is, in the laundering operation. Such an approach is based on a rapid reaction between peroxide and peroxide activator to produce the new species, the peroxyacid. The reaction has to be rapid enough to generate the peroxyacid, with sufficient time for the new species to produce the desired bleaching effect. Also the peroxyacid so produced must have some stability in the laundering solution. The classic method of the preparation of organic peracids is the reaction of the organic acids, for instance, acetic acid, with hydrogen peroxide under mineral acid catalysis. Such reactivity is not noted with the organic acids or, more properly, their anions under the alkaline conditions of laundering.

Under the alkaline conditions necessary for laundering, a mechanism is required which utilizes the peroxide moiety and suitable organic molecules for the formation of organic peracid.

Classic substitution reactions entail attack on an electron-deficient center by an electron-rich group (X^-), with replacement of a less electronegative species (Y^-), that is, a species which is a better leaving group and can better compensate for the negative charge by distribution within its structure. Such an idealized system for peroxide activation is presented below:

$$R\overset{O}{\overset{\|}{C}}-Z + H_2O_2(OOH^-) \longrightarrow R\overset{O}{\overset{\|}{C}}-OOH\ (R\overset{O}{\overset{\|}{C}}-OO^-) + Z^-\ (ZH)$$

This system requires certain characteristics for the Z portion. The peroxide anion must be able to displace the Z portion and do so at a fast enough rate, preferably in the early stages of the laundering operation, to allow maximum reaction time for the peracid to effect good bleaching. Further, this reaction must take place in the alkaline media of laundering, pH 9 to 10, and predominate over the competitive hydrolysis reaction of the activator in such an alkaline medium. The organic activator must be of such a character that the acyl fragment is not bound too tightly and hence is only slowly reactive with peroxide, yet not bound so loosely that the competitive hydrolysis reaction will predominate. The peroxide reaction is the favored one, as evidenced by the literature values for the ratio of bimolecular rate coefficients of hydrogen peroxide to water in reaction with acetic anhydride, where the ratio is 30, and for hydroperoxyl to hydroxide ion in reaction with either benzonitrile, when the ratio is 10^4, or *p*-nitro phenyl acetate, where the ratio is 5×10^2 (8).

A considerable patent literature has sprung up on the use of acyl-bearing molecules for such application. Potential activators have been evaluated in the literature (9) by the addition to a specified detergent solution containing perborate at 60C of an amount of the activator under study, equimolar to the perborate. After a 5-min stir, a suitable aliquot is pipetted onto a mixture of cracked ice and glacial acetic acid. Upon addition of potassium iodide solution, the contents are titrated with thiosulfate solution to the first disappearance of the starch indicator end-point. Under these conditions only the peracid formed oxidizes the iodide. A measure of peracid is obtained and consequently a measure of the utility of the compound under study. Actually the peracids from these acyl molecules have pKa values of 7 to 9, consequently they exist in both the acid and anion form in solution. Of course, such activator evaluation depends upon a reasonable water solubility for the activator under study.

From the broad patent literature, a number of classes of compounds have been shown to have some effectiveness. These classes include acid chlorides, anhydrides, phenolic esters, phosphate esters, and acylated imides, amides, and sulfonamides. The acyl fragment is usually an acetyl or benzoyl group or substituted derivative thereof. The types of bleaches then formed include peroxy acids, such as peracetic and perbenzoic acids.

That there is a systematic logic for activator reactivity with peroxide is demonstrated by the data in Fig. 1. These data were obtained for a representative series of acetyl-type activators, varying only in the previously mentioned Z portion of the molecule. This study was conducted in a buffered pH 10 system under homogeneous conditions. The activator molecules were dissolved in diglyme (the dimethyl ether of diethylene glycol), after which a constant aliquot of solution was added to the stirred solution of perborate predissolved in the buffer. In this manner all systems were kept at 2×10^{-3}M in reactants with 5% by volume of diglyme. Titration for peracid was carried out by using the thiosulfate procedure.

The numbers in parenthesis are the pKa values for the conjugate acids, that is, ZH, of the leaving portion, Z^-, in the reaction scheme. These pKa values at least qualitatively represent the bond strength and leaving group ability of the Z portion. The lower the pKa, the more weakly bound should be the acetyl group. It is noted that a decreased rate of reactivity with peroxide is observed in going from acetic anhydride (conjugate acid is acetic acid with pKa 4.76) up to acetylsalicylic acid (conjugate acid pKa of >13). The two extremes in reactivity are represented by acetyl chloride (conjugate pKa <1) and methyl acetate (conjugate pKa >14). In acetyl chloride is observed a weak bond where hydrolysis predominates; in methyl acetate, so strong a bond that neither type of reactivity is noted.

With activators that are not too susceptible to hydrolysis, reactivity appears to be governed by pH. Thus the higher the pH, the larger the concentration of perhydroxyl ion and the faster the rate of reaction. The data in Fig. 2 bear this out. Here acetylsalicylic

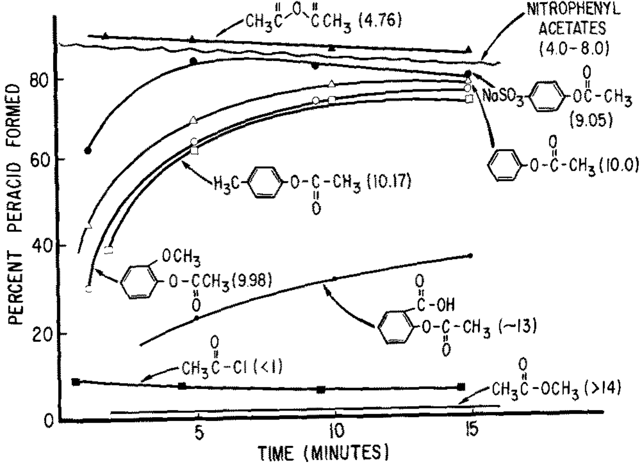


FIG. 1. Acetyl activators.

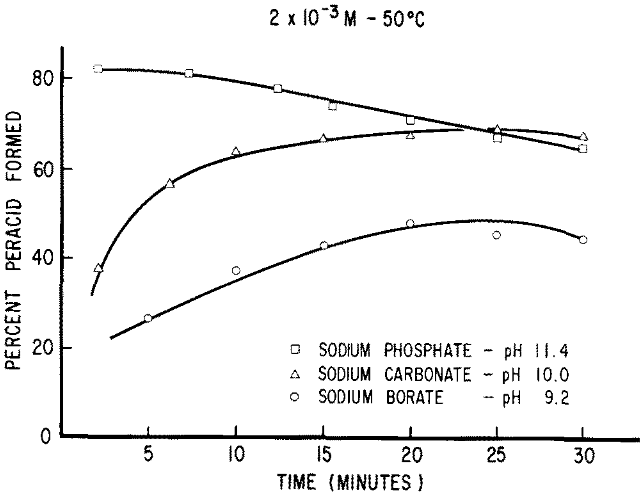


FIG. 2. Reaction of acetyl salicylic acid and sodium perborate.

acid was studied in buffered solutions at 50C by the titration procedure. As can be seen with increased pH, there is an increased rate of reaction.

These results confirm that, under homogeneous conditions, there is a logical sequence for activator reactivity. That a tight balance between hydrolysis and perhydroxyl reactivity exists under practical laundering conditions is demonstrated by the data in Table III. Here N-benzoyl succinimide, which functions as an activator molecule, was evaluated to see the effect of hydrolysis under laundering conditions. As is obvious from the data, hydrolysis of activator is occurring under laundry conditions in the absence of perborate.

Although organic activators have been shown to have effectiveness in improving perborate bleaching, other factors have to be considered in assessing this approach. First, there is the necessity of the use of essentially equimolar amounts of activator to perborate if complete perborate activation is desired. In this case a cost problem is encountered since none of these activators are cheap. Another problem to be considered is whether the activator will dissolve fast enough in the laundering solution to be transformable in the early stages of laundering into the peracid. Of course, another major problem is the incorporation of such an organic molecule into a detergent formula containing perborate or into a bleach product containing just perborate. Since hydrolyzable, peroxide-reactive chemicals are being dealt with, there are many obvious problems in building such formulations.

An attempt to defray the cost of activator systems has been by the use of polyacetylated molecules. A number of activator functions are fused onto the backbone of a single molecule, thereby requiring less of this carrier group. An example of this is triacetyl cyanurate (TACA). This molecule is offered as combining realistic costs, effective bleaching, negligible fabric damage, and minimal attack on dyes. The effect is summarized from the literature in Fig. 3 (10). Based on the recommended weight ratio for the system of 0.8 parts TACA to 1.0 parts of perborate, there is a mole ratio of about 0.5 TACA to 1.0 peroxide. Another advantage is that a TACA-perborate mixture providing 16.6 ppm of active oxygen is germicidally equivalent to 200 ppm solution of available chlorine against *Salmonella typhosa.* One providing 18 ppm active oxygen is germicidally equivalent to 100 ppm available chlorine against *Staphylococcus aureus* (10). Finally repeated launderings of cotton with this system result in low levels of fabric damage, slightly more than detergent alone but much less than with hypochlorite.

TABLE III

N-Benzoyl Succinimide-Influence of Hydrolysis (120F)

N-Benzoyl succinimide (x 10^3 M)	Perborate (x 10^3 M)	Time (min)^a	Final Rd
..	1	....	64.9
1	1	15	63.0
1	1	5	71.7
1	1	0	82.8

[a] Time of N-benzoyl succinimide in presence of detergent solution and stained cloth prior to perborate addition.

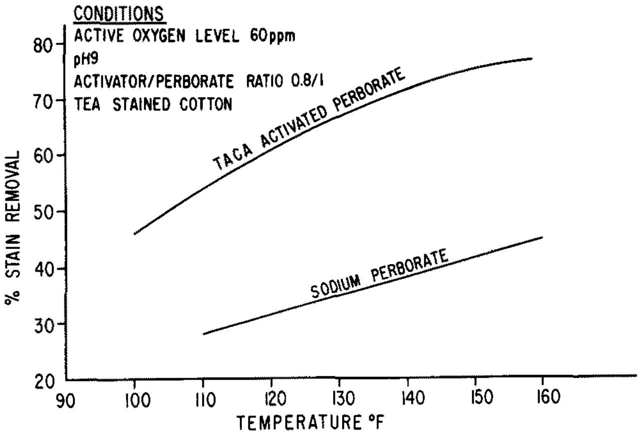


FIG. 3. Effect of temperature on stain-removal effectiveness.

Therefore, in summary, the three common routes to perborate activation, namely, the thermal, metal catalytic, and organic activator, have been covered. The thermal route offers no promise under present conditions in the United States. The second, the metallic catalyst route, although potentially being effective and offering an economically attractive system, is subject to many uncontrollable factors which may not be surmountable. The likelihood of reduction to practical use is uncertain. The third route, organic activators, may eventually reach commercial development in product form. The effectiveness is there with such systems. Only the drawbacks of activator cost and successful formulation into products remain to be overcome.

REFERENCES

1. Powe, W. C., Textile Res. J. *29,* 879 (1959).
2. Powe, W. C., and W. L. Marple, JAOCS *37,* 136 (1960).
3. Kirk, R. E., and D. F. Othmer, Encyclopedia of Chemical Technology, *10,* 49 (1953).
4. Fenton, N. J., J. Chem. Soc. *65,* 899 (1894).
5. Konecny, J. O., and R. E. Meeker (Shell), U. S. Patent 3,156,654 (1964).
6. Hirtz, J. L., and G. Noiriel (Colgate), U. S. Patent 3,211,658 (1965).
7. Wallace, J. C., "Hydrogen Peroxide in Organic Chemistry," Electrochemical Dept., Dupont (1960).
8. Parker, W. P., C. Ricciuti, C. Ogg and D. Swern, J. Am. Chem. Soc. *77,* 4037 (1955); Wiberg, K., Ibid. *77,* 2519 (1955); Jencks, W. P., and J. Carriuolo, Ibid. *82,* 1778 (1960).
9. Davis, T. D., G. C. Hampson, F. R. McDonnell and G. Schmerlaib (Lever Bros.), U. S. Patent 2,955,905 (1960).
10. FMC Company Technical Data Bulletin No. 14, on trisacetylcyanurate.