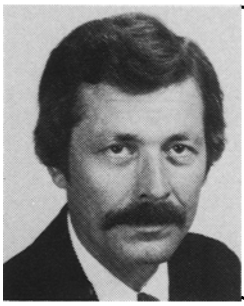

Bleach: Facts, Fantasy, and Fundamentals

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ABSTRACT

Bleaching agents are primary adjuncts of the cleaning process. They can be formulated as separate products for discretionary use or incorporated as an integral part of the cleaning product. The chemistry and expected performance benefits of the various types of commercially available bleaching agents are discussed. The known chemical and environmental factors affecting shelf stability and in-use activity of bleaching agents are reviewed. Attributes for the "ideal" household bleach are also outlined.

INTRODUCTION

The practice of bleaching textiles is at least as old as laundering, for the sun was the primordial bleaching agent. Chemical bleaches in the form of nature-derived chemical substances such as sour milk and alkaline clays were utilized by the textile guilds of the 14th century. Modern chemical bleaching agents had their genesis along with the emerging science of chemistry in the late 18th century with the discovery of chlorine by Scheele. A French chemist, Berthollet, subsequently found that adding caustic potash to a water solution of chlorine gas would produce an effective bleach. An enterprising entrepreneur named Javelle marketed this chlorinated potash solution, and it has been commonly called "eau de javel" ever since.

Use of chemical bleaches is no longer limited to the industrial craftsmen or chemists. For most of the present century, bleach has been utilized in increasing amounts by homemakers as a versatile supplement to household cleaning and sanitizing activities. The bulk of this usage has been and continues to be as an additive in the home laundry process, but significant amounts are also utilized in hard surface cleaning and specialized personal care products. In the U.S. alone, about 6.5 billion loads of household laundry were bleached in 1976 (1). Although the growth rate of the bleach market in the U.S. has been slower in the 1970s than in the two preceding decades, bleach use is not a declining practice. The number of laundry loads that are bleached continues to increase (Fig. 1). The growth rate slightly exceeds the increase in number of household units over the same time period (2).

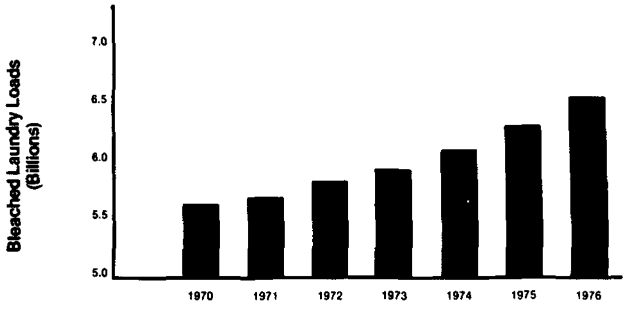


FIG. 1. Laundry bleach usage in U.S., 1970-1976.

DEFINITIONS

There are two types of chemical agents to consider for consumer bleaching products. Of primary importance are the oxidizing bleaches. There are other chemical agents that are commonly called reducing bleaches. These are primarily used as dye stripping agents and are a very small factor in the consumer products marketplace.

Our working definition of household bleaches encompasses those chemical compounds that provide an oxidizing action. The oxidation potential may range from the relatively mild activity of organic oxidants employed in certain personal care products to the more highly reactive halogen-releasing compounds commonly associated with cleaning and sanitizing products.

The term "bleaching" can give rise to semantic confusion among industrial chemists because it has been applied to dissimilar processes in various industries. An edible oil chemist knows bleaching to be a removal of color bodies primarily by means of filtration. A cereal chemist uses oxidizing "bleach" chemicals to accelerate the desired aged characteristics in new-crop flour. A dye chemist may use bleach to either destroy, modify, or stabilize a dye. Textile and paper technologists tend to regard bleaching as a whitening process only, it being a standard procedure for removing visible natural impurities from cellulose pulp and fibers.

For those of us in the household cleaning products business, however, the process of bleaching means more than just whitening. The oxidative action on soils and stains is synergistic with the surface active mechanism of detergents. The chemical combination of bleach and detergents is practically unbeatable for overall removal of a broad spectrum of soils which are common in the household.

The various types of oxidative bleaches exhibit relative differences in aggressiveness, and also some degree of specificity for the types of soils and stains that are most sensitive to the particular oxidizing mechanism. Thus, laboratory proof of the overall performance of household bleaches can involve the testing of almost limitless combinations of bleaching chemicals, associated washing chemicals, and soil/stain complexes. The billions of household usages each year of chemical bleaches attest to consumers obtaining beneficial results over wide-ranging conditions whether or not there is full understanding of the fine points of chemistry taking place.

THE DECOMPOSITION PARADOX

A truism of bleach chemistry is that the bleach compound must be inherently unstable to perform its function. Unlike other chemicals used in the washing process, a bleach must react (literally "decompose") to a state of inactivity for its full effect to be observed. Since these are oxidizing chemicals, the decomposition reaction involves intermolecular electron transfer; the active material gains electrons to produce a less active reaction product.

The paradox, of course, involves the matter of control – how to keep an unstable chemical from decomposing prematurely, but then having it undergo rapid and complete decomposition at the right time. The study of practical bleaching agents, therfore, hinges largely on the observation of decomposition mechanisms, reaction rates, and the influence of the chemical environment in which the agent is placed. Surprisingly, the exact reaction mechanisms and activity rates of some of the most commonly used bleach chemicals are even today not completely understood. The literature yields several credible hypotheses, but some theoretical conflicts have not been fully resolved.

FACTORS INFLUENCING BLEACH ACTIVITY

The influence of the chemical environment on the activity of a bleach is easier to observe than are the theoretical reaction mechanisms. These influences are also of practical importance to detergent specialists who are attempting to maximize the synergistic performance of the bleach and detergent in the washing process.

Four factors have a marked influence on bleaching agent activity, regardless of the type of bleach. These factors are commonly involved in the kinetics of most chemical reactions. They were aptly illustrated by a cartoonist 50 years ago in an industry handbook (3) and are worth reviewing.

1. *Heating:* All bleaches work faster with increasing temperature. Inorganic peroxygen bleaches, for example, are relatively slow and nonaggressive unless the solutions are brought to a near boil.
2. *Contact with some metals:* The catalytic effect of heavy metals, unless closely controlled, is generally regarded as destructive because it speeds the decomposition rate too much. Only traces of metals are needed to create this reaction.
3. *Increasing concentration:* The presence of a greater number of reactive molecules generally yields more activity. The performance response to higher concentration is not necessarily linear, however. Furthermore, with hypochlorite solutions, increasing the concentration can also increase the ionic strength which can hasten autodecomposition.
4. *pH:* Acids speed up some bleaches; alkalis speed up others. The pH influence can be very important and is often dictated by the buffering capacity of other chemicals in the washing solution, not just the pH of the bleaching agent itself.

When all four of these factors are working in concert, the combined effect on chemical activity can be dramatic. Such a maximization is not practical, however, because the dual goal of shelf stability and in-use instability demands a tight balancing of these influences with the directional effect of one factor being countered by another factor. For example, the slower activity resulting from reducing the in-use temperature may be compensated in part by an adjustment of use-solution pH. This pH adjustment is best done by the detergent ingredients because adjusting the pH in the bleach product itself could markedly alter the shelf life of the bleach. The required balancing of factors varies with each type of bleaching agent. The entire matrix of possible factor combinations for optimizing the system can be fairly complex. Additionally, when considering laundry applications, this matrix becomes an overlay of the effects that these same factors have on the detergency attributes of surfactants and builders. Optimization of the combined matrices of bleach and detergent variables involves an even more staggering number of testing possibilities.

TYPES OF HOUSEHOLD BLEACHING AGENTS AND THEIR CHARACTERISTICS

The two broad categories of oxidizing agents most commonly chosen for household bleaching are the peroxygens and hypochlorites. These may be either inorganic or organic compounds. The end-use product form may be either a dry or a dilutable solution. The simplest examples of each category are hydrogen peroxide and sodium hypochlorite, although these are not the only compounds that are commercially offered. Let us look a little closer at the chemistry and performance attributes of each type, for there are relative differences as well as similarities which are of interest.

Hypochlorite Bleaches

Chemical fundamentals: Sodium hypochlorite is by far the most highly commercialized hypohalite bleach. Chemical homologs such as potassium hypochlorite, sodium hypobromite or hypoiodite, and various chlorine oxide solutions have been utilized for very specific applications not related to household laundering. An organic material, potassium or sodium dichloroisocyanurate, is also used in household products including laundry bleaches. Its chemical activity in solution is analogous to sodium hypochlorite since it forms hypochlorite ions or hypochlorous acid on hydrolysis.

The chemical convention for describing the potential oxidizing "strength" of a chlorine type bleach is to measure its "available" or "active" chlorine. (The terminology is not internationally standardized, and literature references can be confusing depending upon their country of origin.) The term is intended to express the potential electron transfer capability of the compound as opposed to actual content of a particular element within the molecule. Because chlorine gains two electrons in decomposing from hypochlorite to chloride salt, the percent "active" chlorine is twice the percentage of mol weight attributable to chlorine. Pure sodium hypochlorite is 95% "active" chlorine; for some chlorine-containing oxidizing agents, an "active" chlorine content of over 100% is possible by this convention.

As stated before, an understanding of bleach reactivity is a matter of knowing decomposition reaction mechanisms and rates in addition to amount of "active" chlorine (electron transfer capacity). This is particularly true of hypochlorite because there are two different spontaneous decomposition paths. For purposes of simplifying what is in reality an only partially understood phenomenon, the two decomposition routes are called the chlorate path and the oxygen path (4,5). The terminology derives from the distinguishing end product of the two observed reactions:

Chlorate Path

$$3\,NaOCl \longrightarrow 2\,NaCl + NaClO_3$$

Oxygen Path

$$2\,NaOCl \longrightarrow 2\,NaCl + O_2$$

In reality, the decomposition of hypochlorite solutions probably proceeds in interrelated degrees along both paths at the same time, and total decomposition observed is the summation of both routes. The factors reviewed earlier as affecting observed bleach activity (i.e., heat, metal ions, ionic concentration, and pH) all play a role in modifying the chemical kinetics to enhance one pathway while subduing the other. For hypochlorite solutions, light can be an additional influencing factor on spontaneous decomposition, the degree of influence varying with intensity and wavelength.

Researchers attempting to study kinetic mechanisms and to quantify the rate constants of the reactions have often reached conflicting conclusions because of the complications of parallel decomposition paths and the sensitivity of the decomposition to many parameters (6-10). Despite this lack of consensus, several hypotheses have emerged as useful guidelines to the practical applications chemist, as follows:

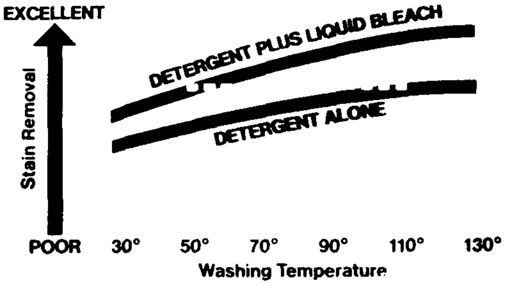
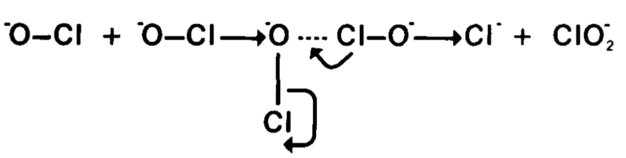


FIG. 2. Stain removal performance.

1. The chlorate path of decomposition is primarily associated with autodecomposition. It is the predominant reaction that is observed when hypochlorite slowly loses its active strength even under relatively favorable storage conditions. What is believed to be happening on a molecular basis might be expressed as one hypochlorite ion attacking another, one chlorine atom acting as an electron donor and another acting as an electron acceptor, such that both lose their "bleaching" capability:



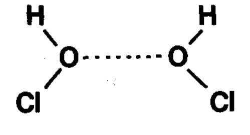
$$^{-}O-Cl + {}^{-}O-Cl \longrightarrow {}^{-}\underset{Cl}{O} \cdots Cl-O^{-} \longrightarrow Cl^{-} + ClO_2^{-}$$

This mechanism probably takes place at a much more accelerated rate in the active bleach bath than during shelf storage. But because this path does not contribute to functional bleaching, the realities of this mechanism have related to the storage stability of the hypochlorite in solution of the period between manufacture and use.

2. The oxygen path of spontaneous decomposition is also observable in product shelf-life testing because it is by this mechanism that an aged, tightly capped bottle will slowly build up pressure from the oxygen gas that is evolved. Raising the temperature or pH (about 13) will accelerate this reaction.

The major interest in this pathway, however, focuses on its relationship to the active bleaching reaction of hypochlorite, since empirical evidence suggests that the end products of the chain reaction that produces functional bleaching are also oxygen and chloride ion. It has been called the "catalyzed" decomposition route because it occurs when heavy metals are introduced as well as when effective oxidation of soils and stains on textiles is observed.

The similarity of end products in these autodecomposition and "catalyzed" reactions may or may not be coincidental. The intermediate steps in the reactions could be quite different because the kinetics are pH dependent. One point of commonality, however, could be the charge transfer mechanism which encourages the oxygen-oxygen interaction. The functional bleaching reaction is optimized in the pH 6 to 8 range where hypochlorite ion and hydrochlorous acid are present in nearly equal amounts. Conceptually, the oxygen-oxygen interaction would be more likely to occur with hypochlorous acid since the hydrogen ions neutralize the negative charge on the oxygen and tend to stabilize the activated complex:



Whether molecular oxygen is ever formed to participate in the oxidation process is only of theoretical interest as long as the complex formed in an intermediate step of the pathway provides this functional benefit.

3. While heat and ionic concentration speed up general chemical activity and thus accelerate all decomposition paths at the same time, pH control can be used to minimize or optimize the productive "active" decomposition with more specificity. This should always be kept in mind when washing chemicals and bleach are used together. The washing chemicals are usually buffered at a pH favorable to detergency, but not necessarily optimum for safe, effective bleaching.

Performance characteristics: In relating the performance attributes of hypohalite bleaches to other types of bleaches, one must remember that all comparisons are within the context of the normal conditions of use. In the U.S., hypochlorites are regarded as more "heavy duty," broader spectrum oxidative agents than peroxygen type bleaches. This viewpoint is supported by empirical evidence from many users. However, this evidence cannot lead to the conclusion that "chlorine" is more effective (or more destructive) than "oxygen" per se. Rather, it should be viewed that hypohalite bleaches are more active than peroxygen bleaches when the associated conditions of use are not highly aggressive. Inorganic peroxygen bleaches need higher temperatures, higher alkalinity, longer time to achieve their optimum performance – conditions more typical of European than of U.S. laundry practices.

Hypochlorite significantly assists in the removal of stains and certain types of soils. It is especially efficacious on protein-based soils such as are found on clothing that comes in direct contact with the body. The oxidation and peptizing of these nitrogen-containing complexes creates smaller soil particles for the surfactant to lift and float away from the textile substrate.

This boost to cleaning is provided even in low temperature washing because the activity of hypochlorite is less susceptible to the temperature drop than is the activity of many detergents. In controlled tests, one can show that stain removal at 27 C (80 F) with hypochlorite bleach included is equivalent to 48 C (120 F) washing with only detergent (Fig. 2). The extent to which bleach usage will substitute for temperature reductions varies with different washing systems and soils, but it is almost always in the positive direction.

One added bonus of a hypochlorite bleach is that it acts as an antibacterial agent, even in room temperature solutions. For many years it was supposed this activity was the result of actual destruction of the proteinaceous cell wall of the microorganism. Some recent theories have been advanced that other effects such as specific disturbance of the cell metabolism by hypochlorite may play a role in the disinfecting process. Regardless of the exact mode of action against the bacteria, the same use conditions that maximize the bleaching and cleaning effects will also enhance the disinfecting efficacy.

One of the traditional concerns about hypochlorite bleach is that it is too aggressive for certain textile fibers and dyes. Certainly this is true if it is misused or if conditions of use are directed toward increasing its aggressiveness when such activity is not really needed. The transition from natural to synthetic fibers and the development of more stable textile dye systems in the last decade has greatly reduced the incidence of unfavorable side effects from the normal use of hypochlorite bleach.

With all of its positive contributions to the laundering process, we could ponder why there has not been more concerted effort by the household products industry to commercialize an all purpose heavy duty washing product that incorporates a hypohalite bleach. It is technically possible to do so, although some chemical compatibility facts do limit formulations. Hypohalites will interact with almost any unprotected nitrogen bond. Thus unstable combinations will be formed with ammonia salts of anionic surfactants, some amides and amine type sequesterants. Ethylene oxide adduct surfactants are also reactive in intimate mixtures with hypochlorite. Minor ingredients such as enzymes, fluorescent whitening agents, perfumes, and colorants often are not tolerant of long storage in the presence of hypochlorite. The organic powder form of hypohalite (e.g., isocyanurate) will be more compatible with other dry ingredients unless moisture is present, but a moisture-free product is also difficult to formulate and maintain.

Even if a clever formulator finds a way around these limitations, there remain some marketing dilemmas. The product must be distributed as a perishable item, because its shelf life will be much shorter than that of a regular detergent. Flexibility of use by the consumer is curtailed, especially as to when and how much bleach is needed for various kinds of soil or stain situations. Additionally, the dry chemicals which must be used to provide a reasonable product shelf life are more expensive than liquid sodium hypochlorite. It is not surprising, therefore, that there has been slow acceptance of a detergent with "built-in" hypochlorite bleach even in the U.S. where allegiance to hypochlorite bleach is the highest in the world.

Peroxygen Bleaches

Chemical fundamentals: Many of the chemical principles governing hypochlorite activity and decomposition are equally applicable to peroxygen bleaches, although there are some notable exceptions. We can best illustrate the chemical kinetics of this class of oxidants by focusing on hydrogen peroxide, the simplest compound in this category.

The final reaction products of alkaline hydrogen peroxide bleaching systems are water and oxygen:

$$\textbf{Net reaction:}\quad 2H_2O_2 \longrightarrow 2H_2O + O_2$$

The hypothesized mechanism for the decomposition chain may be initiated with or without the presence of a catalytic agent. In both instances, the formation of HO and HO_2 radicals is required to facilitate the electron exchange of the oxidation-reduction process. The radicals are formed slowly without the presence of a catalyst by a pathway which can be termed a self-oxidation-reduction reaction:

$$H_2O_2 \rightleftharpoons H^+ + HO_2^-$$

$$HO_2^- + H_2O_2 \longrightarrow HO_2^{\bullet} + HO^{\bullet} + HO^-$$

$$HO^{\bullet} + H_2O_2 \longrightarrow HO_2^{\bullet} + H_2O$$

The effective bleaching system more than likely will reflect the influence of a catalytic agent since even a trace of metal cations or electron-donor "soils" will accelerate the chain reaction as shown below:

$$M^{2+} + H_2O_2 \longrightarrow M^{3+} + HO^- + HO^{\bullet}$$

$$HO^{\bullet} + H_2O_2 \longrightarrow HO_2^{\bullet} + H_2O$$

$$M^{3+} + HO_2^{\bullet} \longrightarrow M^{2+} + O_2 + H^+$$

It should be noted that the reaction rates of acidic solutions of pure hydrogen peroxide are very slow, but are greatly accelerated in alkaline solutions. In other words, the pH effect on peroxygens is the reverse of that hypochlorite: acids speed up hypochlorite, alkalis speed up peroxygens.

Several hydrated or peroxygenated salts that yield peroxide radicals on hydrolysis have been used for commercial bleaches. Examples include:

Sodium perborate tetrahydrate

$$NaBO_3 \bullet 4\,H_2O$$

Sodium carbonate peroxyhydrate

$$2\,Na_2CO_3 \bullet 3H_2O_2$$

Potassium peroxymonosulfate

$$KHSO_5$$

Of these, sodium perborate is by far the most widely used, both for separately added bleaches and as a "built-in" bleach ingredient in detergents.

Over the years, several companies have tried to find chemical ways to boost the activity rate of peroxygen compounds, especially for situations not amenable to near boiling temperatures. Heavy metals such as copper or cobalt have been proposed as catalysts, but these have generally resulted in too rapid a reaction. It requires an arduous balancing act to introduce inhibiting chemicals that will control the catalytic action at the desired rate.

Another route to accelerating peroxygen activity which has been commercialized might be termed the peracetic route. This approach takes advantage of the fact that the organic peroxides such as peracetic acid, CH_3COOOH, are more active at lower temperatures than the inorganic peroxygen salts. There are a number of organic compounds which are capable of being peroxygenated in situ by a hydrogen peroxide source. These include triacetylcyanuric acid (TACA), tetraacetylglycouril (TAGU), and tetraacetylethylenediamine (TAEDA). Under the right conditions, these accelerators do provide noticeable functional improvement to the inorganic peroxygen salts. However, they must generally be used on an equal molar basis with the peroxygen compound, and thus the cost of using two compounds instead of one to achieve more efficacy presents an economic dilemma to the product formulator.

Additional developments in the direction of peroxygen bleaches with increased bleaching activity are the use of organic peroxyacids. In a way, these might be viewed as an extension of the peracetic acid route, but utilizing longer chain mono- and dicarboxylic acids. The peroxygenated versions of these acids can have high activity and rapid decomposition rates; so rapid as to be explosive if not diluted or handled properly. The problems in commercializing these will be cost and processing safety. The organic peroxygen acids which have received the most attention to date are diperoxisophthalic acid, dipthaloylperoxide, and diperoxyazelaic acid.

Performance characteristics: The general performance attributes of peroxygen bleaches relative to hypochlorite bleaches have been discussed. A few points may bear repeating and explaining, however.

The peroxygen compounds currently utilized for household laundry bleaching can be characterized as having "mild" action unless the associated conditions of use are quite aggressive. The trade-off of lesser bleaching efficacy (e.g., soil and stain removal) from more potential safety to dyes and fabrics, increased compatibility with other washing chemicals, and increased storage life is a desired trade-off for many users. Thus, there will probably always be a market for both the "mild" and the "heavy duty" types of bleaches to fulfill the varied needs and practices of the consumer.

Peroxygen bleaches have been incorporated into laundry detergents for decades, and these products continue to have broad acceptance, especially in Europe. The limitations of ingredient compatibility in these formulations are minimal compared to hypochlorite, although some processing and packaging care must be exercised to insure that there is no premature loss of the bleach activity.

The "Ideal" Bleach

As a way to summarize this overview of bleaches, I want to fantasize a bit by describing the "ideal" bleach we would all like to create for the marketplace. I present it as a challenge to any research staff.

The ideal bleach would have all the positive features of both hypochlorite and peroxygen, with none of their common shortcomings. Efficacy of soil and stain removal from fabrics should be at least comparable to that of hypochlorite at 60 C (140 F) regardless of temperature of use. It should be able to perform at very low concentrations for the sake of economy, yet not show any adverse effect on fibers or dyes if grossly misused or spilled indiscriminately on sensitive surfaces. It should work almost instantaneously (5 minutes or less exposure time), then cease its action when the job is done. It should be shelf stable for 1-2 years, not subject to autodecomposition nor prone to react with other cleaning compound ingredients with which it is combined. It would be even more fantastic if it had versatile in-use application possibilities, such as being dispensed in a clothes dryer instead of the washing solution, or sprinkled on a dry surface such as a floor or carpet. And, of course, after meeting all these criteria, it must be inexpensive – probably no higher cost per use than the cost of the detergent associated with the same task.

Almost every one of these parameters contains a paradox from a technical standpoint. But before we discard this description as wishful thinking, let it remind us that balancing the chemistry in such a way as to even partially resolve some of these paradoxes is the way "better" consumer products are born.

Also, examination of these parameters reveals that a surprising number of them are already being met by one or more types of bleaches being offered now to the consumer. Perhaps the futuristic bleach need not be so totally different from the bleach of the present. Chemical facts and fundamentals may give us some restraints, but the creative search for the "magic wand" will continue!

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