Technical News Feature

Selection of Bleaching Agents for Dry Bleaches

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ABSTRACT

Dry bleaches or all-fabric dry bleaches are increasing in usage (7% +, annually, is quoted) because the consumer is seeking fabric and dye safety coupled with good stain removal. Additionally, the consumer wants a product which requires less sorting of fabrics or colors and aids in the cleansing and stain-removal action without color, fabric, or finish damage. The leading bleach ingredients for dry all-fabric bleaches are peroxygen salts. One of the newest of these peroxygens with a good combination of performance characteristics – for bleaching, good stain removal, positive building action, and cumulative whitening – is the advanced FB^{TM} Sodium Percarbonate. This presentation looks at the formulation of dry bleaches, their constituents, and how market needs are met, and examines the properties of the two persalt alternatives.

THE MARKET FOR DRY BLEACHES

Dry bleaches form part of the armory of additives available to those in the pursuit of clean, stain-free washing. Let us first look at some facts about the marketplace.

Table 1 shows the sales value of bleaches, according to a major industry source. While sales of liquid bleach appear to have stabilized, dry bleach is still growing at 7% per year.

The figure for all-fabric bleaches may be understated in terms of today's value, especially if the repositioning of a major product (Biz) into the dry bleach area is taken into account.

The potential market for dry bleach still remains large. In 1973 it was estimated that only one in four laundry loads was bleached. If we look at the position today, the picture has not changed substantially.

There still remains a major potential for sales expansion, not only on the basis of the number of consumers not currently using bleach but also in terms of those loads not bleached at all. The current market for dry bleach is dominated by four brands: Purex, Snowy, Clorox 2, and Miracle White (five, if Biz is considered in the category).

Private-label local and generic brands account for 7-10% of the market; generics are showing a good rate of growth, but still have only a small share.

Therefore, this market still has a large potential for growth.

MARKET POSITION

Since there are many laundry additives, we should look at the needs these products are designed to satisfy. Where a product is positioned in the marketplace, and how it is promoted will be major factors in its marketing success. This in turn will influence formulation and performance characteristics in terms of market claims. We find virtually all current products are considered as wash improvers and brighteners as well as bleaches. The important claim is fabric- and dyestuff-safety.

We see such claims as "all-fabric bleach" . . . "removes stains" . . . "brightener for all washable fabrics" . . . "safe on washable colors" . . . "use on permanent press wash-and-wear synthetic blends" . . ."no chlorine to damage or discolor" . . . "keeps fabrics looking extra bright" . . . "safe for all baby's washables, including fast colors" . . .

From these quotations, we are beginning to develop the criteria for successful products: "no chlorine" "effective" "remove stains" "brightens", and "safe".

DRY BLEACH FORMULATION

We can now start to consider how the formulation is designed to meet consumer needs. The constituents of dry bleaches can be very different, varying from brand to brand, but all dry bleaches need to be looked at as part of the total wash system.

The bleach products must complement the performance of the wide variety of detergents available as well as providing additional cleaning benefits. Most US detergents are designed to be used at a level of ca. 2g/L or 1.25-1.5 cups per load in a washing machine holding 17-20 gallons of water. In fact, the median use is said to be 3/4 cup per load and the machines tend to be overloaded.

This can lead to underbuilt wash conditions in the machine and a loss in cleaning power. The addition of dry bleach helps boost the concentration of those ingredients already found in the heavy-duty detergents (HDD) as well as providing the all-important stain-removal and brightening effects. Dry bleach ingredients, in addition to the bleach component, include builders – phosphates, silicates and soda ash; fillers – salt and sodium sulfate; functional minor ingredients – surfactants, enzymes, fluorescent whitening agents and blueing agents; and consumer satisfiers – perfume and speckles.

The builders provide alkalinity and soften the water, to optimize the HDD activity. Minor ingredients such as enzymes help to remove protein soils; fluorescent whiteners improve brightness and whiteness. Salt and sodium sulfate used as fillers can reduce the formulation cost or balance the physical properties. Perfume is often added to increase consumer acceptance of the dry-bleach product, although the HDD itself will already be perfumed.

The common factor in all products is the presence of a bleach ingredient. The other parts of the formulation may vary.

The balance of ingredients may help to achieve a positioning in the market or to achieve a degree of uniqueness. For example, one product may contain a high level of bleach to make a "concentrated reduced dosage" approach

TABLE I

US Bleach Markets

	Sales ($ million)	% Using
Laundry bleach		
Liquid chlorine	260	72
All-fabric bleach	160	20
Total	420	88
All laundry aids	1,278	95

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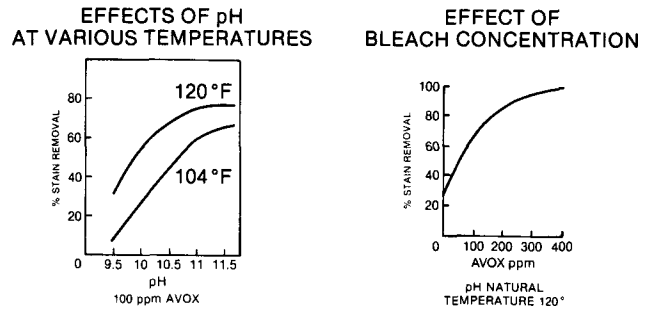

FIG. 1. Effects of pH and bleach concentration on FB™ Sodium Percarbonate. Conditions: wash time, 30 min; detergent concentration, 5g/L; stain, red wine on cotton.

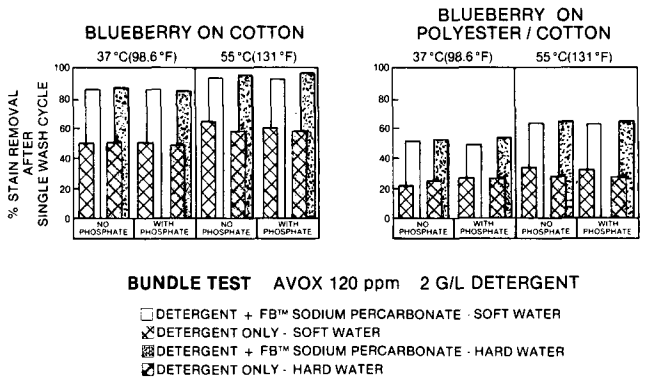

FIG. 2. Bleaching with FB™ Sodium Percarbonate: blueberry on cotton, and blueberry on polyester/cotton.

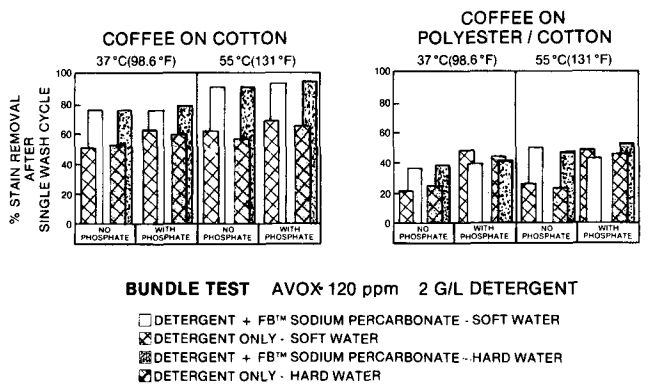

FIG. 3. Bleaching with FB™ Sodium Percarbonate: coffee on cotton, and coffee on polyester/cotton.

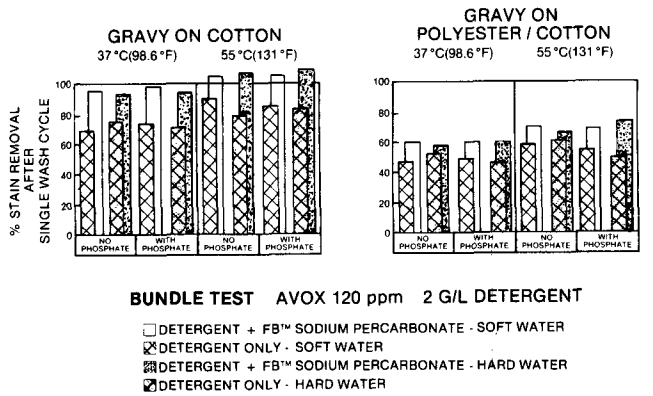

FIG. 4. Bleaching with FB™ Sodium Percarbonate: gravy on cotton, and gravy on polyester/cotton.

to the market. Another might have a higher level of brightener which works well with polyester fiber to claim superiority with this type of fabric.

Since the solid bleach element is the key to all formulations, we need to look at the performance needs. First, the bleach must be fabric- and dyestuff-safe over a wide range of conditions. It must add to the stain-removal performance of the wash load. It needs to be compatible with other ingredients, and to retain its activity. It should also dissolve quickly and must be environmentally acceptable. It is very important that the product should be available and economically viable.

Various alternative substances have been considered and have reached the market. Some we looked at are chlorinated isocyanurates, permonosulfate, sodium perborate tetrahydrate, and sodium percarbonate. However, the only products currently in volume use are sodium percarbonate and sodium perborate.

Dry bleaches based upon chlorinated isocyanurates or potassium permonosulfate have been marketed in the past. They were not entirely satisfactory on the grounds of fabric finish and dyestuff damage and are now little used. If we go back to the primary criterion for a dry all-fabric bleach, it is safe used with clothes. The safety must extend over a wide range, in case of misuse.

The products upon which virtually all dry bleaches in the USA are based are peroxygen salts, which provide a source of active oxygen. These give a more gently bleaching action than either liquid hypochlorite or other alternatives.

This is true not only in the USA but also overseas. There are markets developing for dry bleach in Europe, and well established markets in the Middle and Far East. For example, well over 14,000,000 kg of sodium percarbonate are consumed in making Japan's dry-bleach products.

Of the alternatives in peroxygens, there is a choice of the "traditional" product, sodium perborate, or sodium percarbonate (more correctly, sodium carbonate peroxyhdrate) which has been in commercial production for only a relatively short time in the USA but has a significant share of the dry-bleach market.

FACTORS AFFECTING PEROXYGEN BLEACH PERFORMANCE

In designing a dry bleach, it is important to recognize the factors which will influence the bleaching performance of the active ingredient.

When using peroxygen bleaches, which yield hydrogen peroxide in solution, the usually accepted mechanism involves formation of the perhydroxyl ion. It is this ion, and not some form of "nascent oxygen", which does the bleaching.

Putting it simply, an equilibrium will exist in solution between hydrogen peroxide on the one hand and the hydrogen cation and perhydroxyl anion on the other:

$$H_2O_2 \rightleftharpoons H^+ + [OOH]^-$$

Most conditions favoring the maximum formation of $[OOH]^-$ will favor bleaching, e.g., pH and concentration.

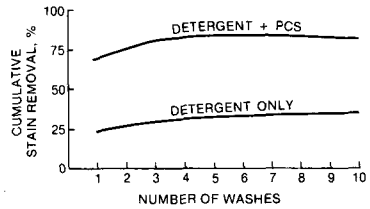

FIG. 5. Bleaching effect of PCS: blueberry on polyester/cotton. Avox 120 ppm, 2 g/L detergent; 20-min washes (TERG-O-TOMETER) @ 130 F water hardness, 150 ppm $CaCO_3$.

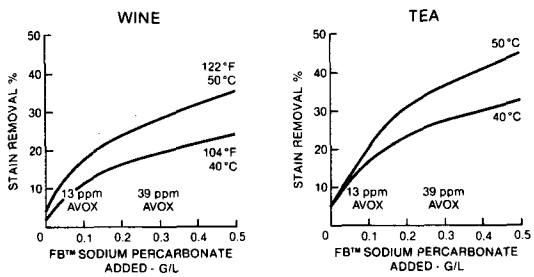

FIG. 6. FB™ Sodium Percarbonate stain removal at lower Avox levels: 15-min wash (TERG-O-TOMETER), 2 g/L nonphosphate detergent.

Less obvious is the fact that, as the $[OOH]^-$ species is used up, the equilibrium moves to the right; time, therefore, becomes an important consideration.

Figure 1 illustrates the importance of some of these effects.

The optimum pH is ca. 10.5. As with almost all chemical systems, temperature increases reactivity. Under some conditions at high pH, undesirable reactions will take place, leading to the loss of the bleaching species to form oxygen and water. Heavy metals, especially iron, catalyze the decomposition of peroxygens. Pack stability and performance of persalt bleaches will be adversely affected if contamination occurs.

Most of our work shows that the optimum level for stain-removal performance with peroxygens will be ca. 100 pm available oxygen in solution. The illustrations which follow involve FB Sodium Percarbonate (made by Interox America), which contains 13% available oxygen.

Time represents another very practical function. The rapid rate of solution for sodium percarbonate produces effective levels of $[OOH]^-$ ions in a short time. Performance of FB Sodium Percarbonate is tailored to the typical 10-15 min US washing machine cycle.

The potential for soak products based on FB Sodium Percarbonate should not be ignored. Here the rapid rate of solubility at low temperatures will again have an advantage. Cold- or warm-water soaking for 1-2 hr, or overnight, will give excellent bleaching.

STAIN-REMOVAL PERFORMANCE

Stain-removal performance is illustrated in Figures 2-4 for blueberry, coffee, and gravy stains on cotton and polyester/cotton. The figures were obtained using a modification of the ASTM bundle test; phosphate and nonphosphate detergents are shown under normal and hard-water conditions at 98.6 F and 131 F.

It can be seen that the stain-removal characteristics are

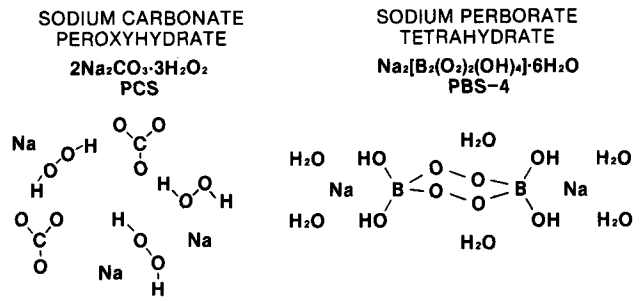

FIG. 7. Structures of sodium carbonate peroxyhydrate and sodium perborate tetrahydrate.

very good and the performance of nonphosphate detergents is improved. Bear in mind that the swatches used were very heavily stained, much more heavily than is likely in practice.

It is also worthwhile stating that the stain removal is cumulative over a number of washes. There are stains which are not moved by repeated washing with detergent alone. Blueberry is a typical example and the effect is shown in Figure 5. This particular test was made in a TERG-O-TOMETER.

The graphs illustrate the good bleaching performance at levels of available oxygen in the 100-ppm range. At lower Avox levels, peroxygens provide a brightening and cleaning effect. The bleach system provides a light bleach on the fabric and also removes stain build-up in the wash solution which, if not eliminated, will lead to redeposition and consequent graying.

Figure 6 shows stain-removal performances at lower concentrations, still effective for the low-level staining encountered in most US wash loads.

PEROXYGEN COMPOUNDS AVAILABLE

Of the two all-fabric peroxygens available, sodium perborate and FB Sodium Percarbonate, Interox America believes the performance and formulating advantages lie with the fluidbed percarbonate. The products are different in structure, as shown in Figure 7. Both compounds liberate available oxygen but they are different chemical compounds.

Both liberate H_2O_2 in aqueous solution. The Percarbonate has been shown to be a peroxyhydrate. The sodium perborate has cyclic peroxygen linkages. Because of the structure differences, the peroxyhydrate will be more sensitive to moisture under package conditions and the perborate more sensitive to heat. Both will be decomposed by heavy metals; therefore, the total formulation must be low in iron and heavy metals. All dry-bleach formulations must be packaged in low-permeability packages or there is a risk of caking or loss of activity. Both need to be added after the formulation has cooled prior to packaging.

There are differences in physical properties. FB Sodium Percarbonate is produced by a fluidbed process and is coated. This gives a compact spheroidal particle. Particle size is controlled within a tight range; the product is dust free. When attrition occurs in handling and processing, the fluidbed product does not break down to give fines in the product or dust in the atmosphere.

Physical characteristics of the two commonly used peroxygen salts are shown in Table II.

The greater concentration of active product, per unit

TABLE II

Comparison of Persalt Properties

	FB™Sodium Percarbonate	Sodium perborate tetrahydrate
Chemical formula	$2Na_2CO_3 \cdot 3H_2O_2$	$NaBO_3 \cdot 4H_2O$
Color	White	White
Form	Microcrystalline granule	Crystalline
Available oxygen	Approx. 13.0%	Approx. 10%
Bulk density	1.0-1.1	0.75-0.8
Solubility (20 C), g/L	120	24
Rate of dissolution, %		
(15 C, 2g/L) 1 min	95.4	23.8
2 min	100.0	31.2
3 min	–	50.5
pH (1% soln)	10.5-10.6	10.2-10.3
Attrition ISO test %	0.5-1.5	8-16
Predominant range of particle size (USS)	25-60	35-100

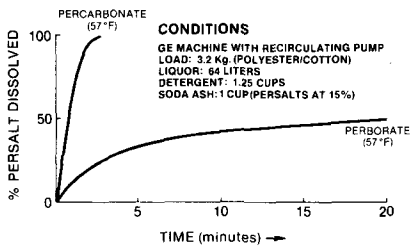

FIG. 8. Rate of solution of persalts. Conditions: GE machine with recirculating pump; load, 3.2 kg (polyester/cotton); liquor, 64 L: detergent, 1.25 cups; soda ash, 1 cup (persalts at 15%).

volume, and the easy flow properties of the Percarbonate are highly valued in the design of "liquid flow" high-concentration bleaches. A major significant difference is shown in the rate of solubility of the products. The rapid solubility of the Percarbonate is very important under cold-water conditions as shown in Figure 8. If the product does not go quickly into solution, benefit of concentration and time is lost in an already short wash cycle.

The rapid solubility, together with the slightly higher pH value in solution and the characteristic peroxyhydrate structure, helps explain the excellent performance profile shown by the Percarbonate and its acceptance in US, Japan, and Middle East dry-bleach marketplaces.

To furnish maximum stain removal and optimum cleaning, dry-bleach compounders should consider the economic and promotional values of marketing concentrated dry-bleach formulations. Availability of such products can assure highest Avox levels for the most efficient laundering and will offer competitive advantages in the marketplace.

FUTURE DEVELOPMENT

Beyond consideration of the current formulations and the availability of a new peroxygen product for helping to meet increasing commercial demands, dry-bleach producers must look to the future. For one thing, formulation options will open up as NTA progresses in the marketplace. For another, is the opportunity to expand the market for concentrated, "liquid-flow", solid, all-fabric bleaches open to those who seek a product different from the current range of dry bleaches. These are already sold in Europe and Japan.

The consumer need for clean clothes and convenient washing will continue, and products to improve wash performance are likely to be even more important. Dry bleaches may need to change and improve. New peroxygen compounds like FB Sodium Percarbonate – or, over the long term, new bleaching species – will continue to be developed to meet the market's needs.

ACKNOWLEDGMENTS

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