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Gray

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[54] BLEACHING AND DETERGENT COMPOSITIONS

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[63] Continuation-in-part of Ser. No. 679,611, Nov. 1, 1967, abandoned.

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[58] **Field of Search** 252/95, 99, 186; 8/111

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[57] **ABSTRACT**

Bleaching and detergent compositions containing a water-soluble peroxide and a water-soluble imide e.g. N-m-chlorobenzoylsuccinimide and N-m-chlorobenzoyl-5,5-dimethyldantoin.

10 Claims, No Drawings

BLEACHING AND DETERGENT COMPOSITIONS

This application is a continuation in part of application Ser. No. 679,611 filed Nov. 1, 1967 for Bleaching and Detergent Compositions now abandoned.

The present invention relates, in general, to compositions advantageously adapted for use in connection with fabric washing and bleaching operations and the like and in particular to the provision of specific compounds and compositions for such purposes, said compositions being characterized in having an exceptionally high order of bleaching activity.

The utilization of bleaching agents as an adjunct to fabric washing operations is, of course, a well established practice and, in many instances, a recognized necessity. Thus, many of the detergent formulations currently available commercially include pre-determined quantities of bleaching agent as an essential ingredient; specific representatives of bleaching agents found to be suitable in this regard are well known in the art being extensively described in the prior art both patent and otherwise and include, for example, the chlorine bleaches, e.g., the alkali metal hypochlorites; active oxygen releasing peroxide compounds, e.g., inorganic persalts such as perborate, percarbonates, perphosphates, persilicates, persulfates, hydrogen peroxide, sodium peroxide and the like.

The peroxide type bleaching agents are, in general, preferred for use being found to be markedly superior as regards capability of providing a fabric having a softer hand, improved absorbency, permanency of whiteness and the like. In contradistinction, other types of bleaching materials, currently enjoying relatively widespread commercial exploitation, characteristically yield fabrics having a pronounced tendency to develop spurious discoloration upon aging, i.e., "yellowing." Moreover, fabrics so treated invariably exhibit significant loss in strength and thus the frequency of bleaching may be such as to severely curtail the useful life of the fabric material.

Despite the cumulative advantages inherent in the use of bleaching agents of the active oxygen releasing type, such materials present the rather serious disadvantage that maximum realization of their beneficial properties can only be obtained ordinarily with the use of elevated temperature ranges, i.e., temperatures in excess of about 185° F. In fact, experience establishes that temperature value approximating 195° F and even higher are mandatory with peroxide bleaches in order to achieve the requisite degree of bleaching activity. The rather critical temperature dependency of the peroxide and especially the persalt bleaches poses a rather serious drawback in view of the extensive public use of washing machines at temperatures ranging from about 120° F. to about 140° F. well below those necessary to render bleaching agents such as the perborates adequately effective for even normal household purposes. Consequently, washing operation requiring comparatively high order of bleaching activity at reduced temperature ranges invariably necessitate the use of bleaching agents other than those of the peroxide type despite the attendant disadvantages necessarily involved, i.e., with respect to possible impairment of fabric strength, inferior resistance to discoloration, etc.

In order to capitalize on the advantageous features characterizing peroxide type bleaching agents, considerable industrial activity has centered around the research and development of means whereby to increase the effectiveness of such materials at reduced temperatures and particularly within the range of from about 120° F. to 140° F. and thus to correspondingly extend their area of effective use.

Perhaps paramount among the techniques thus far promulgated for such purposes are those involving the use of the peroxide bleaching agent in conjunction with one or more auxiliary agents, the latter functioning as activators serving to promote or otherwise augment the bleaching capacity of the peroxide material and thus to make possible the obtention of optimum bleaching activity within the lower temperature ranges.

Although the precise mechanism by which activator compounds of this type function is not self-evident, it has nevertheless been postulated by way of general hypothesis that activator-peroxide interaction leads to the formation of intermediate species which in themselves provide effective bleaching means. In this respect, the activator-peroxide components function as a precursor system by which the in situ generation of species cabable of effective bleaching action is made possible.

Exemplary of the foregoing include activator compounds comprising acylated molecules of various types which, according to theoretical exposition, are alleged to form peracid species as a result of interaction with the bleaching agent, the peracid serving as bleaching agent. As a corollary to the foregoing hypothesis, it has been concluded that the effectiveness of the activator would in turn depend upon the strength of the peracid generated in situ this of course being related to the pKa of such acid. Regardless of the theory involved, experience establishes that significant enhancement of the bleaching capacity of peroxide compounds is obtained with the conjunctive use of auxiliary compounds of this type.

The emergence of detergent and bleaching compositions adapted to cold water washing operations has correspondingly underlined the importance of the function served by the activator compound. As is well known, cold water washing whereby to provide effective detergent and bleaching activity at temperatures approximately those of household tap water presents a plurality of advantages. Thus, the dyestuffs contained in many fabric materials are extremely temperature sensitive i.e., their solubility in aqueous media increase with increased temperatures with accompanying decreases in dyestuff affinity, fastness, etc. Consequently, it becomes necessary in practice to observe special conditions when washing such materials in order to minimize any possibility of dye bleeding, diffusion, etc. which might otherwise occur. It will accordingly be recognized that effective detergent and bleaching action in such circumstances must, of necessity, be attainable at relatively tepid temperature ranges, e.g., within the range of approximately 70° F. to 105° F.

The activator compounds thus far promulgated in the art for such use, although satisfactory in many respects, have nevertheless been found to be subject to one or more serious disadvantages. Perhaps the primary objection relates to the failure of such compounds to provide the requisite degree of bleach activity within the limitations imposed by economical feasible practice and especially at temperatures typical of "cold" water washing. Thus, many of the prior art techniques are characterized in requiring the utilization of the activator and/or bleaching compound in inordinately high concentrations in order to achieve satisfactory results; in other instances, it is found that a given activator is not generally applicable being capable of effective use solely in conjunction with rather specific and delimited types of peroxide bleaching agents. In accordance with the discovery forming the basis of the present invention, it has been ascertained that the utilization of a specific class of compounds in combination with peroxide type bleach and/or detergent compositions makes possible the realization of a high order of bleaching activity at significantly reduced temperatures, i.e., temperatures associated with cold water washing operations.

Thus, a primary object of the present invention resides in the provision of activator compounds specifically and advantageously adapted for conjoint use with peroxide compounds in bleaching and washing compositions wherein one or more of the foregoing disadvantages are eliminated or at least mitigated to a substantial degree.

Another object of the present invention resides in the provision of activator compounds capable of augmenting the bleaching capacity of peroxide compounds to the extent that such materials are rendered feasible for use in connection with washing operations under tepid temperature conditions.

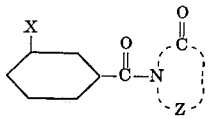
A further object of the present invention resides in the provision of activator compounds capable of synergistically

enhancing the bleaching activity of peroxide compounds, the increase in bleaching activity being obtained despite the use of such activator in relatively low concentrations.

A still further object of the present invention resides in the provision of activator compounds as well as washing and bleaching compositions containing same capable of yielding fabric materials having satisfactory absorbency, softness of hand, resistance to discoloration during wash cycle and upon aging.

Other objects and advantages of the present invention will become more apparent hereinafter as the description proceeds.

The attainment of the foregoing and related objects is made possible in accordance with the present invention which in its broader aspects includes the provision of activator compounds for use in conjunction with peroxide type bleaching agents, said activators comprising compounds of the following formula:



wherein X represents halogen,e.g., chloro, bromo, etc. and Z represents the atoms necessary to complete a heterocyclic nucleus selected from the group consisting of a hydantoin or succinimide.

Particularly beneficial results as regards the attainment of increased bleaching activity with lower concentrations of peroxide compound are obtained with compounds of the above formula wherein X represents chlorine, e.g., N-m-chlorobenzoyl-succinimide and N-m-chlorobenzoyl-5,5-dimethylhydantoin respectively. These particular compounds are singularly characterized in permitting the realization of manifold increases in bleaching activity despite their use in significantly reduced concentrations i.e., concentrations constituting but a fraction of those heretofore required with analogous compounds promulgated in the art for such purposes. Thus, significant improvement in bleaching activity can be obtained with the use of peroxide quantities sufficient to yield a concentration of only 2–4 parts of available oxygen per million parts of wash solution. In general, peroxide quantities sufficient to yield available oxygen concentrations ranging from about 2 to about 20 ppm in wash solution are found to be eminently suitable for the vast majority of laundering operations.

The relative concentration of activator compound and bleaching agent employed is of primary importance in the practice of the present invention since maximum realization of bleaching activity depends critically thereupon. Thus, the activator should be utilized in amounts sufficient to yield a mole ratio of perborate to activator with the range of from about 0.5:1 to about 6:1. Within the foregoing range, specific values may be selected in accordance with the bleaching problem to be negotiated; however, it is usually found that optimization of bleaching activity can be obtained by utilizing a perborate/activator mole ratio which approximate 1:1. In any event, and as will be explained in detail hereinafter, specific and unusual situations may arise dictating departures from use of the optimum ratio in order to suppress, for example, deleterious effects with regard to certain types of dyed fabrics. The bleaching compositions of this invention may be employed in various forms such as powders, tablets and the like with or without additional non-interfering ingredients such as inert fillers e.g. sodium sulfate, sodium chloride, etc, conventional detergent composition components e.g. synthetic detergent, soap, builder salts, soil suspending agents, brighteners, bacteriocides, bacteriostals, anti-oxidants etd, and the like. When used solely for bleaching purposes the composition may consist entirely or substantially (e.g. 50–100 percent) of the peroxygen compound and activator or alternatively there may be added inert filler or other non-interfering ingredients so that the peroxygen-activator combination comprises a minor fraction of the total composition (e.g. 1–50 percent by weight thereof). Where used as a component of a detergent formulation the peroxygen-activator combination may comprise from about 1–75 percent by weight of the total composition with 2–50 percent preferred and 5–40 percent being most preferred. The balance of such formulations comprises the usual ingredients i.e. detergent, builder, etc. in the conventional concentrations e.g. detergent 5–75 percent by weight, builder 5–75 percent by weight, fillers 0–75 percent by weight and minor amounts e.g. 0.1 to 10 percent by weight of other adjuvants such as soil suspending agents, brighteners, anti-oxidants, etc.

EXAMPLES 1–3

The superior bleaching capacity in terms of concentration efficiency will be made readily manifest by reference to the following examples wherein all percentages and parts are given by weight unless otherwise indicated. In each of the examples, testing is carried out at 120° in a tergotometer utilizing sodium perborate of formula weight 154, available oxygen 10 percent and activator in one liter of a 0.15 percent commercial detergent solution having the following composition:

Moisture	10.5 parts
Linear tridecylbenzenesulfonate	21.0 parts
Sodium sulfate	25.8 parts
Pentasodium tripolyphosphate	33.5 parts
Sodium silicate	7.0 parts
Borax (as $Na_2B_4O_7$ 10 H_2O	1.0 parts
Sodium Carboxymethyl cellulose	0.4 parts
Polyvinyl alcohol	0.2 parts
with the remainder comprising antioxidant, brightener, etc.	

In each instance, the test fabric comprises 3 × 6 inch coffee/tea-stained swatches as (cotton). The tergotometer receptacle containing the test swatches and activated perborate detergent solution, is agitated (75rpm) for a period of 10 minutes. After a rinse, the load is dried and evaluated. Reflectance readings are taken both before and after completion of the immersion treatment, the numerical difference between readings being recorded as Δ Rd. The results obtained are itemized in the following table:

TABLE I

Ex. No.	Detergent Composition: Commercial deterg., percent	Na perborate, percent	N-m-cb [1] succinimide activator, percent	P.p.m. avail. O_2	P.p.m. activator	Mole ratio perborate activator	Δ Rd
1	93.2	2.5	4.3	4	70	1:1	4
2	88.3	4.1	7.6	7	130	1:1	7.8
3	84.3	8.4	7.3	15	130	2:1	6.2

[1] Chlorobenzoyl.

As the above data make manifestly clear, efficient bleaching activity is obtained despite an available oxygen concentration of only 4 ppm. Moreover, the reflectance values itemized as ΔRd are markedly superior to corresponding values obtained with analogous activator compounds typical of those described in the prior art when subjected to the identical testing procedure utilizing the identical compo-sitions itemized in the table. The ΔRd value measurement of 4 obtained in example 1 comprises a significantly high value in view of the minimal concentration of available oxygen as well as relatively mild temperature 120° F., at which the testing is carried out. Such value would indicate substantial bleaching activity and especially in view of the somewhat limited period of washing (10 minutes).

As the above data would further suggest, optimum ΔRd values result with the use of a perborate/activator mole ratio of approximately 1:1. Mole ratios considerably in excess of the

equimolar range apparently detract somewhat from the efficiency of the system. The reflectance values obtainable, however, are nevertheless of the first order of significance being markedly superior to many of the compounds heretofore provided.

Thus, the 1:1 mole ratio value would be recommended for most home laundering operations; as a matter of pure economics, excess perborate should be avoided since correlative enhancement of bleaching activity for given increases in concentrations is not attainable thereby.

Within the approximate 1:1 perborate/activator mole ratio range, increased bleaching activity attends the use of the activator system in increased quantities. This aspect is made clear in the above table wherein an approximate two-fold increase in ΔRd is obtained when the relative proportions of activator and perborate and increased correspondingly while maintaining a 1:1 perborate/activator mole ratio.

EXAMPLES 4–6

The procedure in connection with examples 1–3 is repeated in all aspects with the exception that the activator employed comprises N-m-chlorobenzoyl-5,5-dimethylhydantoin. The results obtained are itemized in the following table:

TABLE 2

Ex. No.	Detergent Composition: Commercial deterg., percent	Na perborate, percent	Activator cb dmh [1], percent	P.p.m. avail. O_2	P.p.m. activator	Mole ratio perborate activator	Δ Rd
4	93.2	2.5	4.3	4	70	1:1	4.3
5	88.3	4.1	7.6	7	130	1:1	8.1
6	84.3	8.4	7.3	15	130	2:1	4.9

[1] N-m-chlorobenzoyl-5,5-dimethylhydantoin.

As will be noted, the improvement in reflectance values are similar to those summerized in Table I. Moreover, when compared to the analogous compounds of the prior art, the above data establish marked superiority for the activators of the subject invention; the contrast being particularly striking at available oxygen concentrations approximating 7 ppm. Again, the margin of improvement with respect to ΔRd diminishes with a perborate/activator mole ratio approximating 2:1; similarly, the ΔRd value increases with increasing concentrations of activator and perborate and particularly when the 1:1 mole ratio value is maintained.

As previously explained, optimum realization of the improvements described herein depend vitally on the relative concentrations of perborate and activator. It is envisaged, of course, that within the range previously specified vis 0.5:1 to 6:1 optimum values may vary depending upon the specific application contemplated for the bleach system, i.e., the nature of the fabric, the chemical and physical properties of the colorant affixed to the fabric, etc. This aspect can be made clear by reference to the following examples which illustrate the effects of varying mole ratios of perborate to activator upon the reflectance property, ΔRd, the effects noted being generally representative of those likely to be obtained with other fabric samples. The procedure observed is identical with that described in examples 1–3. The activator material employed in each of the treatments comprises N-m-chlorobenzoylsuccinimide; perborate/activator mole ratios are varied as specified in the table. In order to permit a more comprehensive determination of the effects attending varying mole ratios, the procedure is carried out utilizing detergent to solutions with varying quantities of sodium perborate tetrahydrate to give the specified mole ratio by use of either 1.0×10^{-3}, 5.2×10^{-4}, or 2.6×10^{-4} moles of activator per liter. Again reflectance readings are recorded both before and after the immersion treatment. The results obtained are summarized in the following table:

TABLE 3

Ex. no.	Mole ratio Perborate/ activator	Color Difference Units ΔRd. 1.0×10^{-3} moles activator	5.2×10^{-4} moles activator	2.6×10^{-4} moles activator
7	0.5:1	7.0	6.7	3.7
8	1:1	9.0	7.8	5.0
9	2:1	7.4	4.8	3.6
10	3:1	7.0	4.5	2.5
11	4:1	6.5	3.2	1.6

Also, the effects attending varying mole ratio of sodium perborate to N-m-chlorobenzoylsuccinimide when the available oxygen content from the perborate is fixed at 16 ppm is shown in Table 4.

TABLE 4

Ex. no.	Mole ratio perborate/ activator	Moles of perborate	Color difference units rd.
12	0.5:1	1.0×10^{-3}	9.2
13	0.8:1	1.0×10^{-3}	10.2
14	1:1	1.0×10^{-3}	9.0
15	2:1	1.0×10^{-3}	6.8
16	3:1	1.0×10^{-3}	4.1
17	4:1	1.0×10^{-3}	3.5

As the data in the above tables suggest, optimum improvement in the reflectance property is obtainable with a perborate/activator mole ratio value in the neighborhood of 1:1. This value apparently corresponds to an inflection point with mole ratio values in excess thereof providing somewhat inferior ΔRd. A similar performance behavior was exhibited when N-m-chlorobenzoyl-5,5-dimethyl-hydantoin was used as the activator.

The results itemized in each of the foregoing tables confirm the observation that the activator compounds of the present invention reduce perborate concentration requirements significantly while permitting the realization of synergistic improvement in fabric whitening.

The degree of whitening as a function of concentration of available oxygen, as has been stated previously, is greatly improved in accordance with the present invention. The following examples make clear that synergistic whitening effects attend the use of the activator compound in minimal concentrations and exceedingly low temperature. The general procedure outlined in examples 1–3 is repeated with each of the samples itemized, the activator comprising in each instance N-m-chlorobenzoylsuccinimide. In each case, a 1:1 mole ratio of perborate to activator is employed in conjunc-

tion with a detergent composition suitable for either cold or hot water washing and having the following composition.

Moisture	8.5 parts by weight
Linear tridecybenzensulfonate	12.0 parts by weight
Sodium sulfate	34.9 parts by weight
$Na_5P_3O_{10}$	32 parts by weight
Sodium silicate	5.0 parts by weight
Carboxymethylcellulose	0.5 parts by weight
Fluorescent dye	0.4 parts by weight
Soap	3.1 parts by weight
Polyvinylalcohol	0.2 parts by weight

with the remainder comprising antioxidant, perfume, etc.

TABLE 5

Color Difference Units Δ Rd

Ex. No.	Temperature of	2 ppm Available Oxygen	4 ppm Available Oxygen	8 ppm Available Oxygen	16 ppm Oxygen
18	80	2.0	3.5	4.7	5.2
19	100	2.8	6.7	6.3	6.9
20	120	3.0	5.8	7.8	8.4
21	140	2.6	4.6	9.0	9.4

The above data reveal one of the extremely valuable properties typifying the N-m-halobenzoylimide activators described herein, namely; their capacity to promote at low perborate concentration highly effective bleaching action even at temperatures in the vicinity of only 80° F. Thus, the unique adaptability of such activators to low temperature washing and bleaching operations becomes manifestly clear. Moreover, and of equal importance, the improved bleaching result is readily obtainable with the use of exceeding small amounts of perborate, i.e., amounts sufficient to yield a concentration on the order of only 2–4 ppm of available oxygen in the solution. Thus, reference being made to table 5, a ΔRd value of approximately 6.7 results indicative of a high order of bleaching activity-with an available oxygen concentration of only 4 ppm and at the relatively mild temperature of only 100° F.

The low temperature efficiency of the bleach/activator systems described herein at low concentrations of available oxygen is thus self-evident. It should also be stressed that the N-m-halobenzoylimide activator compounds may be beneficially applied to bleaching operations at higher temperatures, i.e., within the range of from about 120° – 140° F. and higher, by simply increasing the available oxygen concentration. Again, optimum results are assured by the utilization of a mole ratio of perborate to activator in the range of 1:1. Therefore, by merely varying the quantity of perborate, it becomes possible to provide a composition specifically and advantageously adapted to either hot or cold water processing depending upon the requirements of the user. It should also be pointed out that the Δ Rd value of approximately 2 with the use of an available oxygen concentration of only 2ppm, although somewhat reduced in comparison to the other values itemized, is nevertheless highly significant when considered in view of the reduced temperature of 80° F. employed.

It is, of course, of extreme importance in laundering operations that the laundered fabric obtained be devoid of any significant yellowing tendency; thus, optimum whitening effects usually characterize those fabric materials bluish-white in appearance. The appearance of the laundered fabric is of critical importance from this standpoint. However, many of the activator compounds currently available commercially impart to the fabric material an undesired shift in whiteness to yellow. In many instances, this is a direct consequence of the necessity of employing the activator compound as well as perborate bleaching agent in inordinately high concentrations. Similar results are obtained in those instances wherein the activator and/or perborate concentrations are insufficient to afford the requisite level of bleaching activity.

The superior capability of the activators described herein to provide significant bleaching is illustrated in the following examples. In each instance, the testing procedure described in example 1 is followed, i.e., with regard to the detergent compound employed, period of immersion agitation treatment, soiled fabric, etc. In each of the examples, the available oxygen derived from the sodium perborate is maintained at a constant level of 16 ppm. The amount of activator is varied in order to yield the desired mole ratio. Increasing values of Δb, negatively, correspond to greater bluing and thus absence of yellowing, the numerical indicia assigned providing a relative assessment of such property. The activator compound employed comprises N-m-chlorobenzoylsuccinimide. The results obtained are summarized in the following table:

TABLE 6

Ex. No.	Mole ratio perborate/ activator	Δ Rd	Δ b
22	0.5:1	9.2	−3.8
23	0.75:1	10.2	−6.7
24	1:1	9.0	−7.8
25	2:1	6.8	−5.5
26	3:1	4.1	−4.5
27	4:1	3.5	−4.2

As will be noted by reference to the summarized data, optimum values for ΔRd and Δb result with the use of mole ratios of perborate to activator in the vicinity of 1:1. Although such values diminish somewhat with the use of increased perborate/activator mole ratios, such values are nevertheless significant being indicative of superior bleaching as well as capability to provide a fabric having the extremely desirable blue-white appearance. Again, the locus of optimum improvements results with the use of perborate/activator ratios approximating 1:1.

As previously mentioned, specific situations may arise presenting problems somewhat unique in nature, i.e., some difficulties may be encountered as regards the obtention of the requisite level of both ΔRd and Δb. The foregoing situation proves to be particularly problematical with respect to the bleaching and washing of dyed goods, e.g., blue cotton percale. In accordance with the present invention, it has been ascertained that successful negotiation of any such problems can be readily achieved by the employment of the perborate and activator compound in mole ratios approximating 2:1 and higher. In addition, it will usually be found that the use of higher temperatures with such materials is further promotive of bluing effects. However, it should be emphasized that significant bleaching can be effected with dyed fabrics of the aforedescribed nature with the use of reduced temperature ranges, e.g., in the neighborhood of 80° F.

In any event, optimum parameters in a particular instance within the ranges hereinbefore defined such as mole ratio of perborate to activator, temperature, etc., can be readily determined by routine laboratory investigation. However, the above recommended values have been found, in general, to assure the realization of optimum results. The N-m-chlorobenzoylsuccinimide and N-m-chlorobenzoyldimethylhyda-toin activator compounds described in the foregoing examples may be readily and conveniently prepared according to the following procedure:

a. Preparation of N-m-chlorobenzoylsuccinimide To 20.0 g. of succinimide and 40 ml of pyridine, initially at room temperature, was added in drops and with stirring 35.0 g. of m-chlorobenzoyl chloride in a period of about 0.5 hours. After stirring for an additional 0.5 hours, the reaction mixture is allowed to stand for several hours at room temperature. The solidified mass is treated with 100 ml of ethanol and the undissolved crude product removed by filtration. On recrystallization from hot ethanol, about 19.5 g. of N-m-chlorobenzoyl-succinimide, melting point 127.5° – 128° C., is obtained.

b. Preparation of N-m-chlorobenzoyl dimethydantoin To 102.4 g. of dimethylhydantoin and 160.0 g. of pyridine was added with stirring 140.0 g. of m-chlorobenzoyl chloride in a period of about 2.5 hours. Temperature of reaction is between 25 and 62° C. The reaction mixture is next added to 2-liters of water containing 400 ml. of concentrated hydrochloric acid. After allowing to stir for about 10-minutes, the white precipitate is removed by filtration and dried to constant weight. The crude product is recrystallized from ethanol to give N-m-chlorobenzoyl-dimethylhydatoin of melting point 144.5° – 145.5° C.

Results similar to those described in the foregoing examples are obtained when the procedures described are repeated employing in equivalent amounts, in lieu of sodium perborate, one or more of sodium percarbonate, potassium perphosphate, sodium persilicate, and the like. The water-soluble peroxide bleaching agents contemplated for use in accordance with the present invention can be defined as those compounds which give use to hydrogen peroxide when dissolved in water. Thus, such compounds are believed to contain hydrogen peroxide of crystallization.

The compositions described herein can be provided in the form of a bleaching composition or alternatively in the form of a built detergent product. Organic detergents which may be utilized for purposes encompass a relatively wide range of materials and may be of the anionic, non-ionic, cationic or amphoteric types.

The anionic surface active agents include those surface active or detergent compounds which contain an organic hydrophobic group and an anionic solubilizing group. Typical examples of anionic solubilizing groups are sulfonate, sulfate, carboxylate, phosphonate and phosphate. Examples of suitable anionic detergents which fall within the scope of the invention include the soaps. such as the water-soluble salts of higher fatty acids or rosin acids, such as may be derived from fats, oils, and waxes of animal, vegetable or marine origin, e.g., the sodium soaps of tallow, grease, coconut oil, tall oil and mixtures thereof; and the sulfated and sulfonated synthetic detergents, particularly those having about 8 to 26, and preferably about 12 to 22, carbon atoms to the molecule.

As examples of suitable synthetic anionic detergents there may be cited the higher alkyl mononuclear aromatic sulfonates such as the higher alkyl benzene sulfonates containing from 10 to 16 carbon atoms, in the alkyl group in a straight or branched chain, e.g., the sodium salts of decyl, undecyl, dodecyl (lauryl), tridecyl, tetradecyl, pentadecyl, or hexadecyl benzene sulfonate and the higher alkyl toluene, xylene and phenol sulfonates; alkyl naphthalene sulfonate, ammonium diamyl napthalene sulfonate, and sodium dinonyl napthalene sulfonate.

Other anionic detergents are the olefin sulfonates, including long chain alkene sulfonates, long chain hydroxy-alkanesulfonates. These olefin sulfonate detergents may be prepared, in known manner, by the reaction of SO_3 with long chain olefins (of 8-25, preferably 12-21 carbon atoms) of the formula $RCH{=}CHR_1$, where R is alkyl and R_1 is alkyl or hydrogen, to produce a mixture of sultones and alkene-sulfonic acids, which mixture is then treated to convert the sultones to sulfonates. Examples of other sulfate or sulfonate detergents are paraffin sulfonates, such as the reaction products of alpha olefins and bisulfites (e.g. sodium bisulfite), e.g. primary paraffin sulfonates of about 10–20, preferably about 15–20, carbon atoms; sulfates of higher alcohols; salts of α-sulfofatty esters (e.g. of about 10 to 20 carbon atoms, such as methyl α-sulfomyristate or α-sulfotallowate).

Examples of sulfates of higher alcohols are sodium lauryl sulfate, sodium tallow alcohol sulfate. Turkey Red Oil or other sulfated oils, or sulfates of mono- or digly-cerides of fatty acids (e.g. stearic monoglyceride mono-sulfate), alkyl poly (ethenoxy) ether sulfates such as the sulfates of the condensation products of ethylene oxide and lauryl alcohol (usually having one to five ethenoxy groups per molecule); lauryl or other higher alkyl glyceryl ether sulfonates; aromatic poly (ethenoxy) ether sulfates such as the sulfates of the condensation products of ethylene oxide and nonyl phenol (usually having one to 20 oxyethylene groups per molecule preferably two–12).

The suitable anionic detergents include also the acyl sarcosinates (e.g. sodium lauroylsarcosinate) the acyl esters (e.g. oleic acid ester) of isethionates, and the acyl N-meth-yltaurides (e.g. potassium N-methyl lauroyl- or oleyl tauride).

The most highly preferred water soluble anionic detergent compounds are the ammonium and substituted ammonium (such as, mono-, di- and triethanolamine), alkali metal (such as sodium and potassium) and alkaline earth metal (such as calcium and magnesium) salts of the higher alkyl benzene sulfonates, olefin sulfonates, the higher alkyl sulfates, and the higher fatty acid monoglyceride sulfates. The particular salt will be suitably selected depending upon the particular formulation and proportions therein.

Nonionic surface active agents include those surface active or detergent compounds which contain an organic hydrophobic group and a hydrophilic group which is a reaction product of a solubilizing group such as carboxylate, hydroxyl, amido or amino with ethylene oxide or with the polyhydration product thereof, polyethylene glycol.

As examples of nonionic surface active agents which may be used theremay be noted the condensation products of alkyl phenols with ethylene oxide, e.g., the reaction product of isooctyl phenol with about six to 30 ethylene oxide units; condensation products of alkyl thiophenols with 10 to 15 ethylene oxide units; condensation products of higher fatty alcohols such as tridecyl alcohol with ethylene oxide; ethylene oxide addends of monoesters of hexahydric alcohols and inner ethers thereof such as sorbitan monolaurate, sorbitol monooleate and mannitan monopalmitate, and the condensation products of polypropylene glycol with ethylene oxide.

Cationic surface active agents may also be employed. Such agents are those surface active detergent compounds which contain an organic hydrophobic group and a cationic solubilizing group. Typical cationic solubilizing groups are amine and as quaternary groups.

As examples of suitable synthetic cationic detergents there may be noted the diamines such as those of the type $RNHC_2H_4NH_2$ wherein R is an alkyl group of about 12 to 22 carbon atoms, such as N-2-aminoethyl stearyl amine and N-2-aminoethyl myristyl amine; amide-linked amines such as those of the type $R^1CONHC_2H_4NH_2$ wherein R^1 is an alkyl group of about nine to 20 carbon atoms, such as N-2-amino ethylstearyl amide and N-amino ethyl myristyl amide; quaternary ammonium compounds wherein typically one of the groups linked to the nitrogen atom is an alkyl group of about 12 to 18 carbon atoms and three of the groups linked to the nitrogen atom are alkyl groups which contain one to three carbon atoms, including such one to three carbon alkyl groups bearing inert subsituents, such as phenyl groups, and there is present an anion such as halogen, acetate, methosulfate, etc. Typical quaternary ammonium detergents are ethyl-dimethyl-stearyl ammonium chloride, benzyl-dimethyl-stearyl ammonium chloride, benzyl-dimethyl-stearyl ammonium chloride, trimethyl stearyl ammonium chloride, trimethyl-cetyl ammonium bromide, dimethyl-ethyl dilauryl ammonium chloride, dimethyl-propyl-myristyl ammonium chloride, and the corresponding methosulfates and acetates.

Examples of suitable amphoteric detergents are those containing both an anionic and a cationic group and a hydrophobic organic group, which is advantageously a higher aliphatic radical, e.g. of 10–20 carbon atoms. Among these are the N-long chain alkyl aminocarboxylic acids (e.g. of the formula

$$R{-}\overset{R_2}{\underset{|}{N}}{-}R'{-}COOM)$$

the N-long chain alkyl iminodicarboxylic acids (e.g. of the formula $RN(R'COOM)_2$) and the N-long chain alkyl betaines (e.g. of the formula

$$R{-}\overset{+\ R_3}{\underset{R_4}{N}}{-}R'COO^-)$$

where R is a long chain alkyl group, e.g. of about 10–20 carbons, R' is a divalent radical joining the amino and carboxy

portions of an amino acid (e.g. an alkylene radical of one–four carbon atoms), M is hydrogen or a salt-forming metal, R^2 is a hydrogen or another monovalent substituent (e.g. methyl or other lower alkyl), R^3 and R^4 are monovalent substituents joined to the nitrogen by carbon-to-nitrogen bonds (e.g. methyl or other lower alkyl substituents). Examples of specific amphoteric detergents are N-alkyl-beta-amino-propionic acid; N-alkyl-beta-iminodipropionic acid, and N-alkyl, N,N-dimethyl gylcine; the alkyl group may be, for example, that derived from coco fatty alcohol, lauryl alcohol, myristal alcohol (or a lauryl-myristyl mixture), hydrogenated tallow alcohol, cetyl, stearyl, or blends of such alcohols. The substituted aminopropionic and iminodipropionic acids are often supplied in the sodium or other salt forms, which may likewise be used in the practice of this invention. Examples of other amphoteric detergents are the fatty imidazolines such as those made by reacting a long chain fatty acid (e.g. of 10 to 20 carbon atoms) with diethylene triamine and monohalocarboyxlic acids having two to six carbon atoms, e.g. 1-coco-5-hydroxyethyl-5-carboxymethylimidazoline; betaines containing a sulfonic group instead of the carboxylic group; betaines in which the long chain substituent is joined to the carboxylic group without an intervening nitrogen atom, e.g. inner salts of 2-trimethylamino fatty acids such as 2-trimethylamino-lauric acid, and compounds of any of the previously mentioned types but in which the nitrogen atom is replaced by phosphorus.

The detergent composition may further contain one or more water-soluble builder salts which may be either organic or inorganic in nature. Suitable representatives include the following:

Trisodium phosphate,
Tetrasodium pyrophosphate,
Sodium acid pyrophosphate,
Sodium tripolyphosphate,
Sodium monobasic phosphate,
Sodium dibasic phosphate,
Sodium hexamethaphosphate,
Sodium metasilicate,
Sodium silicates, Na_2O/SiO_2 of 1/1.6 to 1/3.2
Sodium carbonate,
Sodium sulfate,
Borax
Ethylene diamine tetraacetic acid tetrasodium salts,
Nitrilotriacetic acid tri sodium salt, etc.

Mixtures of two or more inorganic or organic salts can be used, as can mixtures of inorganic and organic salts.

Particularly preferred herein are water-soluble, alkali metal polyphosphate builder salts. These salts form water-soluble complexes with calcium and magnesium ions found in hard water and thereby prevent the formation of insoluble salts which tend to deposit upon textiles during a washing cycle. Further, such phosphates enhance the detersive efficiency of anionic detergents, aid in controlling sudsing powers and aid in keeping soil suspended in the washing bath after its removal from the soiled textiles.

Various other materials may be included in compositions of the invention, whether in solid or liquid form, by addition in known manner to the aqueous mixtures or to the solidified product. Examples thereof are the higher fatty acid amides such as coconut or lauric monoethanolamide, isopropanolamide and the like; hydrotropic solubilizing agents such as xylene or toluene sulfonates; organic solubilizing agents such as ethanol, ethylene glycol and hexylene glycol; sodium carboxymethylcellulose and polyvinyl alcohol antiredeposition agents; optical and fluorescent brightener materials; coloring agents; corrosion inhibiting agents; germicides; perfumes; a bluing agents; and the like.

Preferred compositions advantageously contain a hydrophobic colloidal cellulosic soil-suspending agent which is soluble or dispersible in water also. The joint use of the combination of the cellulosic compound and polyvinyl alcohol is particularly effective for soil-suspension properties during the washing of a variety of fabrics, including both cotton and synthetic fibers such as nylon, Dacron and resin-treated cottons. The mixtures is used preferably in a total amount of 0.1 to 2 percent by weight of the solids. Preferred cellulosic compounds are the alkali metal salts of a carboxy lower alkyl cellulose having up to three carbons in the alkyl group, such as the sodium and potassium salt of carboxymethylcellulose. Suitable salts are sodium carboxyethylcellulose; the cellulose sulfates and lower alkyl and hydroxyalkylcellulose ethers such as methyl-, ethyl-, and hydroxyethylcellulose.

The proportions of such ingredients are not particularly critical and may be selected so as to conform with established practice. In any event, the detergent agent is usually employed in concentrations ranging from about 2 to about 50 percent by weight of the composition. The builder salts, whether organic or inorganic, are preferably employed in concentrations ranging from about 10 to about 95 percent by weight of the composition. Other ingredients of a conventional nature include perfume and chelating agents.

The desired pH level may be readily achieved by the addition of suitable buffering agents to the bleaching composition, the latter being provided either as a solution or a dry powder, granules, flakes, etc. The bleaching composition may be effectively used at relatively high pH values thereby permitting the conjunctive use of common household laundry soaps as well as detergents specifically devised for preventive bleaching of fiber materials. Of particular usefulness, especially in areas containing high mineral content, is the presence of a chelating agent as, for example, the sodium salts of diethylenetramine pentaacetic acid, ethylene diamine tetraacetic acid, etc. and/or magnesium silicate. For the vast majority of bleaching and/or washing applications a pH within range of from about 6–10 is recommended.

The present invention has been described with respect to certain preferred embodiments thereof and there will become obvious to persons skilled in the art other variations, modifications, and equivalents which are to be understood as coming within the scope of the present invention.

I claim:

1. A bleaching composition consisting essentially of a solid, stable inorganic peroxygen compound and a water soluble N-m-halobenzoyl imide selected from the group consisting of N-m-halobenzoyl succinimide and N-m-halobenzoyl hydantoin and where said halo is selected from the group consisting of bromo and chloro, the mole ratio of said peroxygen compound to said imide being from about 0.5:1 to about 6:1.

2. A composition according to claim **1** wherein said halo is chloro.

3. A composition according to claim **1** wherein said imide compound is N-m-chlorobenzoyl 5,5-dimethyl hydantoin, the peroxygen compound is sodium perborate and the ratio of said perborate to said hydantoin compound is at least 2:1.

4. A composition according to claim **1**, wherein said imide compound is N-m-chlorobenzoylsuccinimide.

5. A composition according to claim **1**, wherein said imide compound is N-m-chlorobenzoyl-5,5-dimethylhydantoin.

6. A composition according to claim **1**, wherein said peroxygen compound is sodium perborate.

7. A composition according to claim **1**, further containing an organic synthetic detergent in amounts ranging from about 2 percent to 50 percent by weight of composition.

8. A composition according to claim **1**, wherein the mole ratio of said peroxygen compound to activator is up to about 2:1.

9. A process for bleaching which comprises contacting the material to be bleached with an aqueous solution containing the composition claimed in claim **1**.

10. A composition according to claim **3** including from 2 to 50 percent by weight of an organic synthetic detergent.

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