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Europäisches Patentamt
European Patent Office
Office européen des brevets

11 Publication number:

**0 224 952
A2**

12

EUROPEAN PATENT APPLICATION

21 Application number: **86202015.3**

51 Int. Cl.⁴: **C11D 3/39** , C11D 3/12 ,
C11D 3/04

22 Date of filing: **17.11.86**

30 Priority: **06.12.85 US 805530**

43 Date of publication of application:
10.06.87 Bulletin 87/24

84 Designated Contracting States:
CH DE ES FR GB IT LI NL SE

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54 **Bleach catalyst aggregates of manganese cation impregnated aluminosilicates.**

57 A bleach catalyst, its incorporation and use in a detergent composition are herein disclosed. The catalyst comprises an aggregate of manganese (II) cation adsorbed onto aluminosilicate particles and a binder to form aggregates of these particles. At least 75% of the aggregates have a diameter size from at least 250 to about 2000 microns. When the catalyst is dispersed in water for 2 minutes at pH 10 and 40°C, less than 5% particles of a diameter 125 microns or higher remain undispersed in water.

EP 0224 952 A2

BLEACH CATALYST AGGREGATES OF MANGANESE CATION IMPREGNATED ALUMINOSILICATES

The invention relates to granulated supported manganese catalysts in aggregate form which, when formulated with peroxygen compounds, promote bleaching of flexible and hard surface substrates.

Dry bleaching powders, such as those for cleaning laundry, generally contain inorganic persalts as the active component. These persalts serve as a source of hydrogen peroxide. Normally, persalt bleach activity in aqueous solution is undetectable where temperatures are less than 100°F and delivery dosages less than 100 ppm active oxygen. The art has recognized, however, that bleaching under such mild conditions may be effectuated through the use of activators.

Manganese (II) salts have been reported to be exceptionally effective in activating persalts under mild conditions. U.S. Patent 4,481,129 discloses bleach compositions containing manganese (II) salts in conjunction with carbonate compounds. U.S. Patent 4,478,733 describes bleach compositions containing manganese (II) salts in conjunction with aluminosilicate cation-exchange materials. U.S. Patent 4,488,980 reports a bleach-beneficial interaction between a condensed phosphate/alkali metal orthophosphate mixture and manganese (II) salts.

Bare heavy metal cations as disclosed in these patents, even when chelated, accelerate wasteful peroxide decomposition reactions that are non-bleach effective. Under alkaline conditions, as when used with laundry-cleaning compositions, metal cations undergo irreversible oxidation and no longer catalyze. Perversely, the peroxide bleaching reaction is most effective at high pH.

Another problem with bare cations such as manganese (II) is that, when utilized for whitening laundry, the free manganese ions deposit on the fabric. Strong oxidants, such as hypochlorites, are frequently included in laundry washes. Manganese ions will react with these strong oxidants to form highly staining manganese dioxide.

Stain problems resulting from free manganese ions have been overcome by binding the heavy metal ion to a water-insoluble support. Thus, European Patent Application N° 0 025 608 reveals a peroxide decomposition catalyst consisting of zeolites or silicates whose cations have been exchanged for heavy metals such as manganese.

In European Patent N° 0 072 166, it was proposed to pre-complex catalytic heavy metal cations with a sequestrant and dry-mix the resultant product, in particulate form, with the remainder of the peroxygen-containing detergent composition. Storage stability was found to be thereby improved. The patent notes that the complex of catalytic heavy metal cation and sequestrant can be agglomerated in a matrix of pyrophosphates, orthophosphates, acid orthophosphates and triphosphates.

While the foregoing systems provide adequate bleaching, three further problems must still be overcome. Upon storage, the catalyst and peroxide bleach particles interact, resulting in loss of bleach activity during storage. Secondly, the catalyst particles are in the form of a fine powder. When blended with detergent granules, the catalyst powder is easily segregated, falling to the bottom of the detergent package. A final problem is the formation of brown manganese dioxide in the detergent package during storage. Not only does the blend become aesthetically unpleasing, but manganese dioxide can deposit on fabric substrates during washing, giving unsightly brown stains.

Consequently, it is an object of the present invention to provide a bleach catalyst formulation in aggregate form that will exhibit improved package storage stability while rapidly releasing active partially manganese-exchanged aluminosilicate particles upon dispersion in water.

Another object of this invention is to provide a detergent composition containing manganese catalyst in aggregate form that exhibits improved storage stability and bleaching performance.

A further object of this invention is to provide an improved method for bleaching substrates, especially fabrics.

A bleach catalyst in aggregate form, exclusive of any peroxy compound within the aggregate, is provided comprising:

(i) from 1 to 99% of a manganese (II) cation adsorbed onto an aluminosilicate support material having an average diameter size of about 2 to 10 microns, the ratio of manganese (II) cation to aluminosilicate support material ranging from about 1:1000 to 1:10; and

(ii) from about 0.1 to 40% of a binder, the amount based on a dry solids weight content of the total aggregate; and

wherein at least 75% of said aggregates have a diameter size ranging from at least 250 to about 2000 microns, said catalyst also leaving less than 5% particles of diameter 125 microns or higher when dispersed in water for two minutes at pH 10 and 40°C, and wherein neither the aggregates nor their components have a pH of more than 10.

The aluminosilicate support material must be one having an average particle diameter size of about 2 to 10 microns (a very fine powder). Larger diameter aluminosilicate particles would have a smaller overall surface area. These would not be as reactive. It has been herein noted that while finely powdered manganese-exchanged aluminosilicate is catalytically active in the wash, if blended as a powder it segregates in the package and adversely interacts with peroxygen compounds upon storage. Aggregation of finely powdered aluminosilicate into larger granules has solved the problem of segregation and storage instability.

Particle size of the catalyst aggregates has, thus, been found to be a crucial factor in overcoming the difficulties of the prior art. At least 75% of the aggregates must have an average diameter ranging from at least 250 to about 2000 microns. Preferably, aggregate diameters should range from 500 to 1500 microns, more preferably 900 to 1200 microns.

Among the aluminosilicates, synthetic zeolites are particularly suitable as the support material. Preferred are those zeolites designated as A and 13X type. These zeolites are sold by the Union Carbide Corporation under the designation ZB-100 and ZB-400, respectively. ZB-100 and ZB-400 have average pore sizes of 4 and 10 Angstroms, respectively. Additional sources of these zeolites are Crosfields Ltd, Philadelphia Quartz, Huber and Ethyl Corporations.

Suitable support materials of another type are the silicoalumino phosphates (SAPOs). These materials are also commercially available from Union Carbide. SAPOs have a wide range of compositions within the general formula $0.0-0.3R(Si_xAl_yP_z)O_z$, where x, y and z represent the mole fractions of Si, Al and P, respectively. The range for x is 0.01 to 0.98, for y from 0.01 to 0.60, and for z from 0.01 to 0.52. R refers to the organic template that is used to develop the structure of the particular SAPO. Typical templates used in preparing SAPOs are organic amines or quaternary ammonium compounds. Included within the SAPO family are structural types such as $AlPO_4-16$, Sodalite, Erionite, Chabazite, $AlPO_4-11$, Novel, $AlPO_4-5$ and Faujasite.

The manganese used in the present invention can be derived from any manganese (II) salt which delivers manganous ions in aqueous solution. Manganous sulphate and manganous chloride or complexes thereof, such as manganous triacetate, are examples of suitable salts.

Finished catalyst will contain from about 0.1 to about 5.5% manganese (II) per weight of solid support. Preferably, the amount of manganese (II) is from about 1 to about 2.5% on an anhydrous basis defined as Mn/anhydrous support + Mn. When dispersed in water, the catalyst should deliver a minimum level of 0.5 ppm manganese (II) ion to the aqueous solution. For instance, if a catalyst has 1 weight % of manganese, then there is required at least 500 milligrams catalyst per litre of aqueous solution.

The catalyst and compositions of this invention may be applied to either flexible or hard substrates such as fabrics, dishes, dentures, tiles, toilet bowls and ceramic floors. Flexible substrates, specifically fabrics, will, however, be focused upon in the subsequent discussion.

A binder is an essential element of the catalyst aggregates. It will be present from about 0.1 to 40% by weight of the aggregate, preferably from about 5 to 20%, ideally from about 5 to 10%. The binder is a water-soluble or water-dispersible material, preferably organic, and will have a pH no higher than 10. Binders may be selected from organic homo-polymers or hetero-polymers, examples of which are starches, cellulose ethers, gums and sugars. Long-chain $C_{10}-C_{22}$ fatty acids and fatty acid soaps may also be suitable binders. Inorganic materials may be used as binders if they meet the pH limitation of no greater than 10, preferably less than 9.5 and more preferably less than 7, and other limitations as herein provided. Illustrative of this category are the so-called glassy sodium phosphates of the molecular structure: $Na_2O_4P-[Na]_2P]_nPO_3Na_2$, wherein the average value of n is from about 10 to 30. Silicates are unacceptable as binders because their pH is greater than 10.

Starches are preferred because of their very favourable combination of good binding and fast water-dispersing properties. Starches usually occur as discrete particles or granules having diameters in the 2 to 115 micron range. While most starches contain from 22 to 26% amylose and 70 to 74% amylopectin, some starches, such as waxy corn starches, may be entirely free of amylose. It is intended to include within the term "starch" the various types of natural starches, including corn starch, potato starch, tapioca, cassava and other tuber starches, as well as amylose and amylopectin separately or in mixtures. Furthermore, it is also intended that such term stand for hydroxy-lower alkyl starches, hydroxyethyl starch, hydroxylated starches, starch esters, e.g. starch glycolates, and other derivatives of starch having essentially the same properties.

Several modified starches are particularly preferred as binders. These include Nadex 320 ®, a white corn dextrin of low viscosity, and Capsul ®, a waxy dextrin hydrophobic derivative, also of low viscosity. Nadex 320 ® and Capsul ® are commercially available from The National Starch and Chemical Company, Bridgewater, New Jersey, U.S.A.

Gums and mucilages are carbohydrate polymers of high molecular weight, obtainable from plants or by synthetic manufacture. Among the plant gums that are of commercial importance may be mentioned arabic, ghatti, karaya and tragacanth. Guar, linseed and locust bean are also suitable. Seaweed mucilages or gums such as agar, algin and carageenan are also within the binder definition.

Among the synthetic gums that are the most favoured are the carboxymethyl celluloses such as sodium carboxymethyl cellulose. Other cellulose ethers include hydroxypropyl cellulose, methyl and ethyl celluloses, hydroxypropyl methyl cellulose and hydroxyethyl cellulose.

Among the organic homo-polymers and hetero-polymers are a multiplicity of materials. Commercially available water-soluble polymers include polyvinylpyrrolidone, carboxyvinyl polymers such as the Carbopol[®] sold by B.F. Goodrich Chemical Company and the polyethylene glycol waxes such as Carbowax[®] sold by the Union Carbide Corporation. Polyvinyl alcohol and polyacrylamides are further examples.

Polyvinylpyrrolidone is a particularly useful binder. Commercially, it is available from the GAF Corporation under the designation PVP K-15, K-30, K-60 and K-90. These products differ in their viscosity grades, the number average molecular weights being about 10,000, 40,000, 60,000 and 360,000, respectively. PVP K-30 and K-60 are the preferred binders.

When modified starches are employed as the binder, they can be incorporated at levels up to about 40% of the total granule weight. Although acceptable granules can be obtained with modified starches at 5-10% concentration levels, it was surprisingly found that at higher binder levels the dispersion rate increased compared to the 5-10% levels. An increase in the level of these binders beyond the minimum required for granulation leads to a dramatic improvement in dispersion despite simultaneous decrease in granule porosity. The effect is similar with polyvinylpyrrolidone.

Binders within the definition of this invention must hold together the aluminosilicate particles in an agglomerate that is free-flowing and non-sticky. Free-flowing properties may be measured by the DFR test as outlined in U.S. Patent 4,473,485 (Greene), herein incorporated by reference. Furthermore, suitable binders are those which provide for coherent agglomerates difficult to crush under ordinary finger pressure.

Another major criterion identifying both binder and resultant agglomerates is their readiness to disperse in water. A Dispersion Test for evaluation of this property has been devised which provides good reproducibility. The percent non-dispersible particles is determined by placing 5 grams of sample agglomerate in 500 millilitres deionized water held at 40°C and at a pH of 10. After stirring for two minutes, the solution is drained through a 120 micron diameter screen. Subsequently, the screen is dried and weighed. Less than 5% by weight of the original sample should remain on the screen. Greater amounts are deemed unacceptable. Failure to adequately de-agglomerate in water means the active manganese (II) on zeolite catalyst will not, to its fullest extent, desorb and contact the peroxygen compound. Bleaching efficiency is thereby impaired.

Laundry bleach compositions are also disclosed by this invention. Besides the agglomerated manganese (II) adsorbed aluminosilicate particles, a peroxide source is necessary. Suitable peroxy compounds include the inorganic persalts which liberate hydrogen peroxide in aqueous solution. These may be water-soluble perborates, percarbonates, perphosphates, persilicates, persulphates and organic peroxides. Amounts of peroxy compound in the dry bleach powder should range from about 5 to about 30%. At least 30 ppm active oxygen should be delivered by the persalt to a litre of wash water. For instance, with sodium perborate monohydrate, this represents a minimum amount of 200 mg per litre of wash water.

The ratio of active oxygen generated by peroxy compound to manganese (II) ion in aqueous solution ranges from about 1000:1 to 1:1000, preferably 1000:1 to 1:10.

Phosphate salt stabilizers are suggested for combination with the dry laundry bleach powders. Suitable stabilizers include the alkali metal salts of tripolyphosphate, orthophosphate and pyrophosphate. Amounts of phosphate stabilizer should range from about 5% to about 35%. Preferably, they should be present from about 10% to 15%. In aqueous solution, the phosphate stabilizer level should be at least 10 ppm, the ratio of stabilizer to peroxy compound being from about 10:1 to 1:10.

Surface-active detergents may be present in an amount from about 2% to about 50% by weight, preferably from 5% to 30% by weight. These surface-active agents may be anionic, nonionic, zwitterionic, amphoteric, cationic or mixtures thereof.

Among the anionic surfactants are water-soluble salts of alkylbenzene sulphonates, alkyl sulphates, alkyl ether sulphates, paraffin sulphonates, alpha-olefin sulphonates, alpha-sulphocarboxylates and their esters, alkyl glycerol ether sulphonates, fatty acid monoglyceride sulphonates and sulphonates, alkyl phenol polyethoxy ether sulphonates, 2-acyloxy-alkane-1-sulphonates and beta-alkoxyalkane sulphonates. Soaps are also useful as anionic surfactants.

Nonionic surfactants are water-soluble compounds produced, for instance, by the condensation of ethylene oxide with a hydrophobic compound such as alcohol, alkyl phenol, polypropoxy glycol or polypropoxy ethylene diamine.

Cationic surface-active agents include the quaternary ammonium compounds having 1 to 2 hydrophobic groups with 8-20 carbon atoms, e.g. cetyl trimethylammonium bromide or chloride, and dioctadecyl dimethylammonium chloride.

A further exposition of suitable surfactants for the present invention appears in "Surface Active Agents and Detergents", by Schwartz, Perry & Berch (Interscience, 1958), the disclosure of which is incorporated herein by reference.

Detergent builders may be combined with the bleach compositions. Useful builders can include any of the conventional inorganic and organic water-soluble builder salts. Typical of the well-known inorganic builders are the sodium and potassium salts of the following: pyrophosphate, tripolyphosphate, orthophosphate, carbonate, bicarbonate, silicate, sesquicarbonate, borate and aluminosilicate. Among the organic detergent builders that can be used in the present invention are the sodium and potassium salts of citric acid and nitrilotriacetic acid. These builders can be used in an amount from 0 up to about 80% by weight of the composition, preferably from 10% to 50% by weight.

Apart from detergent-active compounds and builders, compositions of the present invention can contain all manner of minor additives commonly found in laundering or cleaning compositions in amounts in which such additives are normally employed. Examples of these additives include: lather boosters, such as alkanolamides, particularly the monoethanolamides derived from palm kernel fatty acids and coconut fatty acids; lather depressants, such as alkyl phosphates, waxes and silicones; fabric-softening agents; fillers; and, usually present in very minor amounts, fabric-whitening agents, perfumes, enzymes, germicides and colorants.

The following examples will more fully illustrate the embodiments of the invention. All parts, percentages and proportions referred to herein and in the appended claims are by weight unless otherwise indicated.

Examples 1-9

Catalyst Preparation

A total of 5000 grams manganous chloride tetrahydride were dissolved in 100 litres of distilled water. A separate vessel was charged with a slurry of 100 kilograms zeolite (Crosfields DB10) in 102 litres of water. The slurry pH was adjusted to between 9.0 and 9.5 with sulphuric acid. The manganese solution was fed into the zeolite slurry. Exchange was allowed for 45 minutes.

An Eirich Intensive Mixer (Model RV 02) was charged with 3 kilograms of the dried manganese exchanged on zeolite and with 1.153 kilograms of a 25% (by weight) aqueous PVP K-30 solution. The Eirich rotor and pan were operated at 26.2 metres/sec. and 65 rpm, respectively. Water was added until a total moisture level of about 35% was reached. Agglomeration was observed to occur between about 3 to 8 minutes into the blending, the time being dependent upon the amount and timing of water addition.

Thereafter, the agglomerated product was dried in an Aeromatic STREA-1 fluid bed dryer - (manufactured by the Aeromatic Corporation). Target moisture level was 12.5% water or less. The original khaki colour of the starting zeolite changed to antique white after being dried to the proper moisture level.

Table I outlines agglomeration reactants and properties of the resultant particles. Preparation of product in Examples 2-9 was essentially identical to that of Example 1 detailed above.

Example 2 uses sodium silicate as the binder. Silicate is unacceptable because the pH is about 12, which causes manganese oxidation visually observed as brown particles. Agglomerates prepared with silicate were poorly dispersible and have unacceptable browning properties.

Examples 3-7 illustrate agglomerates with various modified starch binders. Examples 7-9 illustrate the effect of increasing binder level on dispersion and porosity. As the binder level is increased, dispersibility increases but porosity decreases.

TABLE IAgglomerates Prepared with the Eirich Intensive Mixer

				Rosin-				
				Rammler	Distri-		Porosity	
		g of Mn		Average	bution		(cc Hg	
10		Exchanged		Particle	Coef-	% Non-	intru-	
	Ex.	Zeolite	Solution	Size	ficient	disper-	ded	
	N°	Binder	Added	Added	(n)	sible	/gm)	
				(/um)				
15	1	10% PVP	3000	1153 g of	1606	2.42	0	-
		K-30		25% soln.				
	2	5% RU	1000	352 g of	846	3.35	>90	-
		Silicate		5% soln.				
20	3	5%	3000	546 g of	870	1.77	49.6	-
		Purity		25% soln.				
		Gum BE (R) *						
25	4	10%	3000	1153 g of	1443	2.14	21.4	-
		Purity		25% soln.				
		Gum BE (R) *						
30	5	10%	3000	1153 g of	1480	0.83	9.0	-
		Nadex		25% soln.				
		320 (R)						
35	6	10%	3000	1153 g of	875	1.44	12.2	-
		Capsul (R)		25% soln.				
	7	10%	3000	1153 g of	893	2.17	8.0	0.2194
		78-0059*		25% soln.				
40	8	20%	3000	1025 g of	883	2.10	5.1	0.1110
		78-0059*		60% soln.				
	9	40%	3000	2343 g of	684	1.86	1.0	0.0
45		78-0059*		60% soln.				

* Both Purity Gum BE ® and 78-0059 are converted waxy starches soluble in cold water. Purity Gum BE ® is a hydrophobic derivative of starch with a low-medium viscosity; 78-0059 is a stabilized starch of low viscosity; both are products of the National Starch Corporation.

Example 10

The present Example illustrates the effects of various modified starch levels as they relate to dispersibility and bleach effectiveness. Table II shows that the bleaching obtained using catalyst aggregates with 5% or less non-dispersibles is statistically better than where the non-dispersibles are higher than about 5%. For instance, 10% starch 78-0059 gave 8.0% non-dispersibles, while 20% and 40% of starch 78-0059

in the otherwise identical aggregate formulation gave non-dispersibles of 5.1 and 1.0%. A statistically better bleaching was obtained with the 78-0059 starch formulations of 5.1 and 1.0% non-dispersibles than with 8.0% non-dispersibles. Similar results were obtained in comparison of 10% and 40% binder levels using Capsul ®, Purity Gum BE ® and Nadex 320 ®.

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TABLE II

Dispersibility and Bleaching Data for Catalysts with Various Binders

	<u>% Binder</u>	<u>Binder Type</u>	<u>% Non-Dispersibles</u>	<u>Bleach Performance</u>
				<u>ΔR_d/Dunc*</u>
	10%	78-0059	8.0	7.88 $\pm$ 0.57/B
20	20%	78-0059	5.1	9.46 $\pm$ 0.77/A
	40%	78-0059	1.0	9.20 $\pm$ 0.32/A
	10%	Capsul ®	12.2	8.78 $\pm$ 0.32/B
25	40%	Capsul ®	1.0	9.98 $\pm$ 0.42/A
	10%	Purity Gum BE ®	21.4	8.17 $\pm$ 0.32/B
30	40%	Purity Gum BE ®	2.3	9.53 $\pm$ 0.56/A
	10%	Nadex ®	9.0	8.38 $\pm$ 0.47/B
	40%	Nadex ®	$\sim$ 0	9.62 $\pm$ 0.39 /A

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* Dunc refers to a Duncan statistical analysis. Those mean values with a different letter (i.e. A vs.B)are statistically different.

** Bleach tests were performed in accordance with the procedure outlined in Example 11.

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Example 11

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A single-step heavy metal ion exchange and catalyst granulation is herein described. An Eirich Intensive Mixer RV 02 was charged with 3.0 kg Crosfields DB10 zeolite powder and 1.2 kg of a 25% aqueous solution of PVP K-30 binder containing 20 g concentrated 12N sulphuric acid. The mixture was churned at a rotor tip speed of 26.2 m/s and bowl speed of 60 rpm. A manganese sulphate aqueous solution of 121 g manganous sulphate and an equal amount of water were slowly added thereto. Exchange occurred under mixing over a period of 6-8 minutes. The resultant agglomerates were dried in a fluid bed drier for about 0.5 hours at 80°C. Final product water content was between 7 and 11%.

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Bleaching tests were conducted with a 4-pot Terg-O-Tometer from the U.S. Testing Company. Wash solutions were prepared from distilled water with hardness ions added to provide 60 ppm of calcium and magnesium (2:1),defined on a calcium carbonate basis. The wash volume was 1 litre. Temperature was maintained at 40°C. Agitation was provided throughout a 14-minute wash period.

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Bleaching was monitored by measuring reflectance of a dry cotton cloth (4" x 6"). Prior to bleaching, the cloth had been uniformly stained with a tea solution and washed several times in a commercial detergent. Reflectance was measured on a Gardner XL-23 Reflectometer.

The catalyst, prepared in the one-step procedure, was blended (0.151 gram catalyst delivering 2.0 ppm manganese ion) with 1.158 grams of detergent base powder and 0.391 gram sodium perborate monohydrate. The change in reflectance for the single step adsorption/ granulation was essentially identical - (about 7 units) with the two-step process outlined in Example 1. Hence, bleaching effectiveness was not impaired by eliminating one of the steps.

Example 12

Illustrated here is the effect of the average aggregate diameter size on storage stability of sodium perborate when these components are packaged together.

The catalyst aggregates were formed, according to the process of Example 1, from 86.38 parts zeolite, 3.62 parts manganous chloride and 10 parts PVP K-30 binder. Catalyst (0.151 grams) and detergent powder containing 0.391 grams sodium perborate monohydrate were blended together. A 1.7 gram sample of the detergent blend was placed in an open Petrie dish and stored at 80°F/80% relative humidity over an 8-day period. Samples were measured for percent available oxygen (Avox %) using a Kyoto Auto-Titrator. Avox measurements were taken at the beginning of the experiment and after the 8-day storage period. There were also visual inspections to note any discolouration and gross physical changes. Results of this test are shown in Table III.

TABLE III

	U.S.	Particle	Initial*	Final		Catalyst
	Mesh Size	Size		Avox %		Visual
		(Microns)	Avox %	(+ Std. Dev.)	Loss %	In- spection
	10 to 14	1405 to 2000	3.43	3.10±.018	.33	Granular, light brown
	25 to 35	500 to 700	3.43	2.47±.209	.86	Granular, darker brown
	60 to 80	177 to 250	3.43	0.56±.212	2.87	Sludge, very dark brown. Not granular.

* The initial available oxygen reading of 3.43±.1% is the mean of three replicate runs.

The results in Table III show that storage stability improves with increasing size of the agglomerated particle. Loss of available oxygen (2.87%) is significant for particle sizes of 177-250 microns. When the particles are between 500 and 2000 microns, the blend is satisfactorily stable (Avox loss 0.86%). Table III also reports that agglomerated particles in the range 177-250 microns cause the detergent blend to turn dark brown. Original granular material was observed to have turned into sludge. The larger particle size agglomerate containing detergent blend also exhibited some colour darkening. However, discolouration was not severe and the granular quality of the blend remained.

The foregoing description and Examples illustrate selected embodiments of the present invention and in light thereof variations and modifications will be suggested to one skilled in the art, all of which are in the spirit and purview of this invention.

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Claims

1. A bleach catalyst in aggregate form, exclusive of any peroxy compound within the aggregate, comprising:

10 (i) from 1 to 99% of a manganese (II) cation adsorbed onto an aluminosilicate support material having an average diameter size of about 2 to 10 microns, the ratio of manganese (II) cation to aluminosilicate support material ranging from about 1:1000 to 1:10; and

(ii) from about 0.1 to 40% of a binder, the amount based on a dry solids weight content of the total aggregate; and

15 wherein at least 75% of said aggregates have a diameter size ranging from at least 250 to about 2000 microns, said catalyst also leaving less than 5% particles of diameter 125 microns or higher when dispersed in water for two minutes at pH 10 and 40°C, and wherein neither the aggregates nor their components have a pH of more than 10.

2. A bleach catalyst according to claim 1, wherein the particle diameter size ranges from 500 to 1500 microns.

3. A bleach catalyst according to claim 1, wherein the binder is selected from the group consisting of starches, cellulose ethers, gums and sugars.

4. A bleach catalyst according to claim 1, wherein the binder is a long-chain C₁₀-C₂₂ fatty acid or soap thereof.

25 5. A bleach catalyst according to claim 1, wherein the binder is a modified starch.

6. A bleach catalyst according to claim 1, wherein the binder is polyvinylpyrrolidone.

7. A bleach catalyst according to claim 5, wherein the modified starch is present in an amount from about 5 to about 40%.

8. A bleach catalyst according to claim 1, wherein the aluminosilicate support material is a synthetic zeolite having a pore size of from about 4 to about 10 Angstroms.

30 9. A bleach catalyst according to claim 1, wherein the aluminosilicate support material is a silicoalumino phosphate.

10. A bleach catalyst according to claim 1, wherein the amount of manganese (II) cation is present in an amount from about 1 to about 2.5% per weight of aluminosilicate support material, on an anhydrous basis.

35 11. A bleaching composition comprising:

(a) a peroxy compound; and

(b) a bleach catalyst according to claim 1,

wherein the ratio of active oxygen generated by the peroxy compound to manganese (II) ion in aqueous solution ranges from about 1000:1 to 1:1000.

40 12. A bleaching composition according to claim 11, wherein the peroxy compound is sodium perborate.

13. A bleaching composition according to claim 11, further comprising an inorganic phosphate salt stabilizer in an amount from about 5 to 35% by weight of the total composition.

14. A bleaching composition according to claim 13, wherein the phosphate stabilizer is chosen from the group consisting of tripolyphosphate, orthophosphate, pyrophosphate and mixtures thereof.

45 15. A bleaching composition according to claim 11, further comprising from about 0.1 to 98% of laundry detergent adjuncts selected from the group consisting of surfactants, builders, fabric softeners, enzymes, inorganic fillers, colorants, lather boosters and mixtures thereof.

16. A method for bleaching a substrate comprising placing the substrate into water and treating with a composition comprising:

50 (a) a peroxy compound present in an amount to deliver at least 10 mg active oxygen per litre to the wash solution; and

(b) a bleach catalyst according to claim 1 which delivers at least 0.5 ppm manganese (II) cation per litre wash solution.

17. A method according to claim 16, further comprising an inorganic phosphate salt stabilizer present in an amount to deliver from about 0.05 to 0.30 grams per litre wash solution.

55 18. A method according to claim 17, wherein the phosphate salt is selected from the group consisting of tripolyphosphate, orthophosphate, pyrophosphate and mixtures thereof.

19. A method according to claim 16, wherein the peroxy compound is a sodium perborate salt.

20. A method according to claim 16, wherein the composition further comprises from about 0.1 to 98% of laundry detergent adjuncts selected from the group consisting of surfactants, builders, fabric softeners, enzymes, inorganic fillers, colorants, lather boosters and mixtures thereof.

21. A method according to claim 16, wherein the substrate is selected from fabrics, dishes, dentures,
5 tiles, toilet bowls and ceramic floors.

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