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LOW TEMPERATURE BLEACHING COMPOSITION
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ABSTRACT OF THE DISCLOSURE

A stable dry catalyst powder for enhancing the bleaching action of water-soluble inorganic percompounds at low temperatures of 20-50° C. Comprising a metal-ion of a transition element and a water-insoluble or hardly soluble powdered carrier, processes for the preparation thereof and percompound bleaching compositions containing the catalyst powder.

The invention relates to ion/carrier catalysts, to processes for the preparation of ion/carrier catalysts and to bleaching compositions containing these catalysts. In particular, the invention relates to ion/carrier catalysts which affect the bleaching action of inorganic precompounds to such an extent that effective bleaching at relatively low temperatures, e.g. 20-50° C., can be achieved and to their preparation in a suitable and stable form and to their use in bleaching compositions. Such catalysts can be advantageously used in bleaching compositions containing inorganic percompounds, e.g. perborates or persulphates, to obtain low-temperature bleaching and find particular use in scouring powder formulations containing inorganic percompounds.

It is known that certain cobalt and manganese salt solutions when freshly adsorbed on a suitable carrier, such as the alkaline carbonates of calcium, magnesium, zinc or cadmium, exercise a highly catalysing effect on the bleaching action of hydrogen peroxide. Such freshly prepared systems when mixed with a hydrogen peroxide solution have a bleaching effect on certain dyestuff solutions at room temperature.

Known low-temperature bleaching compositions generally contain a chlorine-releasing compound, such as dichlorocyanuric or trichlorocyanuric acid, which has the disadvantage of spreading a disagreeable chlorine smell, which persists for some time after use, especially on the skin, and the further disadvantage of sometimes attacking the fibres of textiles, especially of some finished fabrics. Another disadvantage connected with compositions based on chlorine bleaches is their instability on storage, resulting in a decrease of bleaching effect. These disadvantages are not present to the same extent with bleaching compositions based on inorganic percompounds, such as perborates or persulphates. However, inorganic percompounds are relatively inactive bleaching agents at low temperatures, e.g. 20-50° C. Their bleaching effect increases with increasing temperature and attains its maximum at the boil.

It is an object of the invention to prepare stable catalysts as a dry powder having a free moisture content of less than 15%, preferably 1-5%, which can be incorporated in bleaching compositions containing inorganic percompounds and particularly in scouring powder bleach formulations containing inorganic percompounds.

It is also an object of the invention to provide low-temperature bleaching compositions which are effective in the removal of persistent stains, e.g. tea stains, from hard surfaces, such as dishes, tiles and the like, and which are

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also useful for bleaching stains on fibrous materials, such as finished and unfinished textile fabrics.

Another object is to provide detergent compositions especially for dishwashing containing inorganic percompounds having low-temperature bleaching properties.

A further object is to provide scouring powder compositions containing inorganic percompounds, e.g. sodium perborate, having a bleaching effect comparable with those compositions containing chlorine bleaches.

The catalysts according to the invention comprise a metal ion adsorbed on a suitable inorganic carrier. The metal ions themselves in a non-adsorbed form may or may not have any effect on the bleaching activity of the inorganic percompound. However, when suitably adsorbed on suitable carriers these metal ions increase the bleaching activity to a large extent. It has been found that the metal ions of the transition elements in the periodic system especially those having an unpaired electron spin, such as Co^{2+} , Mn^{2+} , Ni^{2+} , Cr^{3+} , Mo^{2+} , or Cu^{2+} are particularly effective. The carriers which can be advantageously used may be any water-insoluble or slightly soluble compound of Zn, Cd, Ca, Mg, Al, Sn, Be, Ti, Sb, Bi or SiO_2 .

Of these possible combinations the most active catalysts are found when Co^{2+} is adsorbed on: zinc silicate; titanium dioxide or hydroxide; tin dioxide; antimony trioxide; aluminium oxide, hydroxide or silicate; alkaline zinc carbonate; alkaline cadmium carbonate; cadmium carbonate, silicate or oxide. The metal-ion content may be from 1-100 mg. or more per gram catalyst, and preferably from 20-60 mg./g. It goes without saying that the catalysts according to the invention are also effective to aid the bleaching action of inorganic percompounds on coloured solutions at low temperature.

The catalysts according to the invention may be prepared in the following ways:

(a) By dry-mixing a finely-divided powdered salt, e.g. CoCl_2 , containing the metal ion, with the finely-divided carrier in such a way that a homogeneous mixture is obtained, in which both substances are in very good contact.

(b) By adding an aqueous solution containing the metal ion, e.g. CoCl_2 solution, to the required amount of finely powdered carrier. Water is then added and the whole mixture is stirred until a paste-like substance is obtained. The product is then dried at temperatures up to about 100° C.—vacuum may or may not be applied—preferably at temperatures of 40-60° C. in a vacuum of 1-15 mm. Hg. Much higher temperatures may also be applied, depending on the type of catalyst, although it is not advisable since it would affect the catalysts activity.

(c) By freeze-drying the paste-like substances as described in (b), at temperatures of -50° to -0° C. in a vacuum of 0.01-1 mm. Hg.

The catalysts obtained by the aforementioned methods assist bleaching at low temperatures (20° C. or even lower), as well as at higher temperatures, with sodium perborate and/or with other inorganic percompounds including percompounds, such as Du Pont's "Oxone" (a triple salt consisting of potassium permonosulphate, potassium hydrogen sulphate and potassium sulphate in the approximate molecular ratio of 2:1:1).

It is desirable that the bleaching compositions should give an alkaline solution, preferably one having a pH value of between 7 and 11.

It has been found that catalysts prepared according to the process of the present invention can be stored for some time without losing their activity. They can be dry-mixed with inorganic percompounds to form low-temperature bleaching compositions, preferably at weight ratios of between 1:1 and 1:8. Such mixtures when incorporated in normal detergent compositions enable the latter

to bleach effectively at relatively low temperatures. It has also been surprisingly found that the catalysts obtained from the freeze-drying process (process (c)), especially those with zinc compound carriers, are much more active than the catalysts prepared from the same compounds according to process (a) or (b). Their activity, however, decreases on storing under normal room conditions to values approaching those of catalysts prepared according to the other processes of the invention. By a suitable coating of the particles it would be possible to retain his extremely high activity originally obtained. Catalysts prepared with carriers having a particle size of 30–52 mesh (British Standard Sieve) are especially suitable for coating.

The catalysts prepared according to the processes of the invention can be mixed with inorganic percompounds e.g. sodium perborate, to form stable low-temperature bleaching compositions. They can also be incorporated in detergent powder formulations having a percompound content of up to 30% and also in scouring powder compositions with a percompound content of 1–20%, preferably 5–15% of sodium perborate. When used in scouring powder formulations it is preferable that the catalyst be added to the powder as the last component under thorough mixing. It is also preferable that the moisture content of the detergent powder or scouring powder be as low as possible.

In order to avoid unwanted colouring of the bleaching solution and of the object to be bleached, which may be caused by the catalysing metal ion, sequestering agents may be incorporated in the bleaching composition, e.g. sodium hexametaphosphate. Other condensed phosphates, particularly sodium tripolyphosphate, appear to reduce the catalysts' activity.

Example 1

Catalysts having a cobalt content of approximately 4% (40 mg./g. catalyst) were prepared in the following ways:

(a) 100 g. finely powdered zinc silicate (100 mesh—British Standard Sieve) and 19 g. $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ were mixed together in a mortar so that a homogeneous mixture was obtained. The zinc silicate was previously dried in an oven at 80° C. under vacuum for one hour.

(b) To 200 g. finely powdered zinc silicate (100 mesh—British Standard Sieve) a solution of 38 g. $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ was added in 180 ml. water and the mixture was stirred so that a homogeneous paste was obtained. Part of the paste was then dried in a vacuum drier at 40° C. and 10 mm. Hg for 5 hours. The product obtained by powdering the granules in a mortar had a free moisture content of approximately 1.5%.

(c) The other part of the paste was dried at a temperature of less than –20° C. and at a pressure of 0.05 mm. Hg. The moisture content of the product was approximately 1.5%.

Example 2

A number of scouring powder compositions were prepared containing sodium perborate and catalyst prepared according to Example 1. For purposes of comparison two compositions were also prepared, one without catalyst and the other containing the metal ion without a carrier.

TABLE I

	Parts by Weight			
	I	II	III	IV
Sodium dodecylbenzenesulphonate.....	9.0	9.0	9.0	
Silica.....	72.0	65.5	82.5	
$\text{NaBO}_3 \cdot 4\text{H}_2\text{O}$	8.5	15.0	8.5	
Catalyst, containing 4% Co^{2+}	4.0	4.0	-----	
Urea.....	3.0	3.0	-----	
Sodium hexametaphosphate.....	3.5	3.5	-----	

Composition III to which is added 0.16% Co^{2+} as CoCl_2 without a carrier.

These compositions were tested at room temperature for the bleaching of tea stains on unglazed tiles (Royal Sphinx Maastricht, 15 x 15 cm.) by applying them as a paste-like substance to the tile surface. The following test method was used:

The reflectance of a tea-stained tile was measured. 10 grams powder were mixed with 7 ml. distilled water and stirred for 30 seconds. The mixture was poured on the tile surface. After a contact time of 1 or 2 minutes the paste was rinsed from the tile surface with running tap water for at least 10 seconds. After standing in the air for about 24 hrs. the reflectance of the tile was measured again. In the following table the increase in reflectance of the tile surface after treatment is given. From this table it can be seen that the type of carrier used is an important factor.

TABLE II

Composition	Carrier	Increase in reflectance percent after contact time of	
		1 min.	2 min.
I.....	Zinc silicate.....	27	42
	Cadmium carbonate.....	27	29
	Stannic oxide.....	20	24
	Antimony oxide.....	27	30
	Zinc silicate*.....	26	30
II.....	Zinc silicate.....	27	42
III.....	No catalyst.....	3	11
IV.....	No carrier.....	0	5

*Catalyst prepared by dry-mixing. The other catalysts were prepared by process (b).

Example 3

The first four of the compositions referred to in Table II above were stored at room temperature in closed vessels for two months and their bleaching effect again determined in the same way as described in Example 2. The following results show that the compositions retained their bleaching activity during storage:

TABLE III

[Results obtained after storage for 2 months]

Composition	Carrier	Increase in reflectance (percent) after contact time of	
		1 min.	2 min.
I.....	Zinc silicate.....	26	39
	Cadmium carbonate.....	30	31
I.....	Stannic oxide.....	22	23
	Antimony oxide.....	27	28

What is claimed is:

1. A process for the preparation of a stable dry catalyst powder for enhancing the bleaching action of water soluble inorganic percompounds at low temperatures in which an aqueous solution of a salt containing a metal-ion selected from the group consisting of the transition elements in the periodic system is added to a powdered carrier selected from the group consisting of water-insoluble or hardly soluble compounds of Zn, Cd, Ca, Mg, Al, Sn, Be, Ti, Sb, Bi and SiO_2 to form a homogeneous mixture and the mixture is thereafter dried to a moisture content of less than 15%.

2. A process for the preparation of a catalyst powder according to claim 1, in which the drying is carried out at temperatures not exceeding 100° C.

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3. A process according to claim 1, in which the drying is carried out under a vacuum of 1 to 15 mm. Hg and at a temperature of 40–60° C.

4. A process according to claim 1, in which the drying is carried out in the form of freeze-drying at a temperature of –50° to –0° C. and at a vacuum of 0.01 to 1 mm. Hg.

5. A low temperature bleaching composition consisting essentially of a mixture of the catalyst powder consisting essentially of metal-ion selected from the group consisting of the transition elements in the periodic system which is adsorbed on or intimately mixed with a powdered carrier selected from the group consisting of water-insoluble or hardly soluble compounds Zn, Cd, Ca, Mg, Al, Sn, Be, Ti, Sb, Bi and SiO₂, the metal-ion content being from about 1 to 10 milligrams per gram of catalyst powder, and a water-soluble inorganic percompound, the weight ratio between the catalyst powder and the water-soluble inorganic percompound being from about 1:1 to about 1:8.

6. A detergent powder bleach and cleansing composition,

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for use in the presence of water, consisting essentially of the composition defined by claim 5 in amounts such that the water soluble inorganic percompound content is up to about 30 percent by weight of said composition.

7. A detergent and scouring composition, for use in the presence of water, consisting essentially of the low temperature bleaching composition defined by claim 5 in an amount such that the water soluble inorganic percompound content is from about 1 percent to about 20 percent by weight of said composition.

References Cited

UNITED STATES PATENTS

3,156,654	11/1964	Konecny et al.	252—99
3,207,696	9/1965	Shephard et al.	252—186
3,211,658	10/1965	Hertz et al.	252—99

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