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Description

The present invention relates to a process for the preparation of solid photoactivator preparations containing sulfonated zinc and/or aluminium phthalocyanines as the photoactivators, and to the preparations thus obtained, which are stable on storage.

Sulfonated zinc and aluminium phthalocyanines are known as excellent photoactivators which can be employed mainly as photo-bleaching agents, and, if appropriate, also as agents having an antimicrobial action. Cf., for example, US-A-3,927,967, 4,094,806, 4,033,718, 4,256,597, 4,256,598, 4,318,883, 4,166,718, and 4,311,605; and EP-A-47,716. These sulfonated zinc and aluminium phthalocyanines are employed, for example, as photo-bleaching agents in detergents of various kinds.

Hitherto, considerable difficulties have been encountered in preparing useful commercial forms of the said photoactivators. The phthalocyanine-sulfonates are obtained from synthesis in a relatively impure state. As a rule, they contain up to 30% of organic and inorganic byproducts. The latter are mainly salts such as NaCl and Na₂SO₄. The amount of organic byproducts present is, for example, up to 15% and comprises a large number of compounds, some of which have not been identified. These byproducts are extremely undesirable, since they can, for example, impair the action of the photoactivator.

Attempts have been made to remove these byproducts by chemical means. However, the results have not been able to give full satisfaction. The aqueous solutions obtained in this manner have still contained an excessively large amount of byproducts, have not contained the photoactivator in the high concentration desired and have also not been adequately stable on storage. A further disadvantage of these liquid formulations has been that they have frequently gelled, that is to say their viscosity has increased. This undesired effect has often resulted in the solutions becoming gel-like and scarcely pourable any more. This problem has been encountered particularly in the case of sulfonated aluminium phthalocyanine. A further disadvantage, in principle, of liquid commercial forms is

that they require relatively large volumes and thus create transport problems.

If, on the other hand, the said photoactivators are used in the dried powder form obtained from synthesis, disadvantages are also encountered: these powders tend to evolve dust, are not adequately stable on storage and also contain the undesirable impurities described above. Their solubility in cold water and resistance to abrasion are also not satisfactory. In addition, such powders are hygroscopic. An aqueous solution prepared therefrom tends to gel, just like the liquid formulations.

It was therefore the object of the invention to find, for the said photoactivators, a commercial form which does not have the disadvantages described above. The object consisted particularly in finding a solid, dust-free commercial form which is stable on storage and contains as little as possible in the way of organic impurities.

It has been found, surprisingly, that the objects mentioned above can be achieved by passing a crude solution of the said photoactivators through a specific, modified, semi-permeable membrane, and subjecting the resulting concentrated aqueous solution to a gentle drying process, preferably a granulation process. Membrane separation processes are known, for example, from DE-A-2,204,725, 2,805,891 and 2,948,292, EP-A-0,041,240 and EP-A-39,782. European Published Patent Application 37,382 describes a process for the preparation of solid dye preparations, in particular preparations containing reactive dyes, by means of a membrane separation process, various auxiliaries being added, if required.

None of the said publications describes or suggests that solid photoactivator preparations which have a very high stability on storage and a high bulk density, which are not hygroscopic and do not agglomerate and have an excellent solubility in cold water and which, surprisingly, contain extremely little in the way of interfering organic impurities (compared with the dye preparations of the state of the art) and which form non-gelling solutions with water are obtained by the process according to the invention.

The process according to the invention for the preparation of solid photo-activator preparations containing sulfonated zinc and/or aluminium phthalocyanines as the photoactivators is characterised in that a crude solution containing the said photoactivators is passed through a semi-permeable, asymmetric membrane having a pore diameter of 0.1 to 50 nm which consists of a cellulose acetate fundamental framework modified by reaction with an ionic compound containing reactive groupings, or which consists of a fundamental framework which contains polyacrylonitrile or a copolymer formed from acrylonitrile and other ethylenically unsaturated monomers and which has been modified by reaction with hydroxylamine and subsequent reaction with a polyfunctional monomeric compound, a polyfunctional polymer and an ionic compound containing reactive groupings, and the resulting concentrated photoactivator solution is then dried under gentle conditions, it being possible to add, before drying, extenders and/or surface-active substances customary in the detergent industry.

The semi-permeable membranes which can be used in the process according to the invention are intended to retain higher-molecular substances, while ensuring a high flow of water and dissolved substances of low molecular weight, for example salts, such as sodium chloride, sodium sulfate, potassium chloride, ammonium sulfate, sodium phosphate, potassium sulfate or sodium acetate, or low-molecular impurities, for example unreacted or partially decomposed starting materials. They are, however, also intended to be able to separate differentially charged ions.

The retention or removal (cut-off level) is determined by the molecular weight and/or the ionic charge. This so-called membrane hyperfiltration is also known as reverse osmosis and is related to ultrafiltration. This term is to be understood as meaning separation processes within the molecular range.

The membranes which can be used in accordance with the invention are semi-permeable, ionic, asymmetric membranes having pores of 0.1 to 50 nm diameter. They have a cut-off level of, for example, 300 to 500. Membranes having a cut-off level of 400 to 500 are particularly suitable for the process according to the present invention. They permit water and

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dissolved substances which, by virtue of their molecular sizes, are below the removal level (cut-off level) to pass through at high rates per unit area and at a low to medium pressure. Pressures of, for example, 10 to 100 bar, preferably 10 to 30 bar and especially 20 to 30 bar, are used in accordance with the invention. The pressure can be exerted, for example, by means of a pump.

The desalting effect can be up to 70% or more, without loss of photoactivator, in one filtration process. In the course thereof the volume of the solution of retained substances (the concentrate side) decreases correspondingly and the concentration of the retained fraction increases.

If a further reduction in the low-molecular component is desired, this can be achieved without difficulties by repeating the process one or more times after diluting the retained solution or suspension with water, advantageously to its initial volume. The separation can also be carried out continuously by adjusting the inflow rate of the water to that of the removal of permeate.

The membranes which can be employed in accordance with the invention contain a fundamental framework which is composed of cellulose acetate or polyacrylonitrile or a copolymer of acrylonitrile and other ethylenically unsaturated monomers and which has been modified in the manner described above. Above all, membranes based on cellulose acetate have proved successful from a technical point of view.

Suitable reactive reagents containing an ionisable group are colourless and coloured compounds, for example ionic reactive dyes, which can belong to various classes, such as anthraquinone, azo or formazan dyes. Suitable colourless compounds are, for instance, derivatives of 4,4'-diaminostilbene-2,2'-disulfonic acid, for example 4,4'-bis-(4,6-dichlorotriazin-2-yl)-aminostilbene-2,2'-disulfonic acid and similar compounds. The following may be mentioned as reactive groups which make it possible to attach these reagents to the starting polymers: carboxylic acid halide groups, sulfonic acid halide groups, radicals of α - β -unsaturated carboxylic acids or amides, for example radicals of acrylic, methacrylic,

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α -chloroacrylic or α -bromoacrylic acid, and acrylamide radicals, and radicals of, preferably lower, halogenoalkylcarboxylic acids, for example chloroacetic acid, α,β -dichloropropionic acid or α,β -dibromopropionic acid; radicals of fluorocyclobutanecarboxylic acids, for example trifluorocyclobutanecarboxylic or tetrafluorocyclobutanecarboxylic acid; radicals containing vinylacyl groups, for example vinylsulfone or carboxyvinyl groups; radicals containing ethylsulfonyl ($-\text{SO}_2\text{CH}_2\text{CH}_2-\text{OSO}_2\text{OH}$ or $-\text{SO}_2\text{CH}_2\text{CH}_2\text{Cl}$) or ethylaminosulfonyl ($-\text{SO}_2\text{NHCH}_2\text{CH}_2\text{OSO}_2\text{OH}$) groups and halogenated heterocyclic radicals, such as, for example, radicals of dihalogenoquinoxalines, dihalogenopyridazones, dihalogenophthalazines, halogenobenzthiazoles or, preferably, halogenated pyrimidines or 1,3,5-triazines, such as, for example, monohalogenotriazines, dihalogenotriazines, 2,4-dihalogenopyrimidines or 2,5,6-trihalogenopyrimidines. Suitable halogen atoms in the radicals mentioned above are fluorine, bromine and especially chlorine atoms.

Examples of suitable ionisable groups are sulfato groups, sulfonic acid groups, sulfonamide groups, carboxylic acid groups, carboxamide groups or hydroxyl, thiol, isocyanate and/or thioisocyanate groups, ammonium groups formed from primary, secondary or tertiary amino groups and hydrogen, or quaternary ammonium groups and also phosphonium or sulfonium groups. Reactive compounds (reactive dyes) containing sulfonic acid, carboxylic acid or ammonium groups are preferred.

Particularly advantageous results are achieved in some cases using compounds containing sulfonic acid groups. Polymer membranes which are particularly valuable and extensively applicable are those which have been modified by means of an azo dye containing sulfonic acid groups. The azo dye can also contain a metal, for example copper, linked in a complex.

Membranes composed of (partially acetylated) cellulose acetate can be modified, for example, directly by reaction with the reactive ionic compounds mentioned previously, in particular anionic reactive dyes (cf, for example, DE-A-2,505,254).

A further modification of cellulose acetate can ... (sic), for example, by

subsequent chemical reaction (in the sequence indicated) with 1) a polyfunctional monomeric compound containing at least two functional groups (for example cyanuric chloride); 2) a polyfunctional oligomer or polymer (for example polyethyleneimine); and 3) an ionic compound (for example an ionic reactive dye, reactive groupings and ionic groups as indicated) (cf, for example, European Published Patent Application 26,399).

The polyfunctional monomeric compound preferably contains at least 2 functional groups. Suitable compounds are cyclic carbonic acid imide-halides, isocyanates, isothiocyanates or N-methylol compounds, halogenodiazines or halogenotriazines, such as, for example, cyanuric halides (cyanuric chloride) or trihalogenopyrimidines or tetrahalogenopyrimidines (tetrachloropyrimidine) being particularly suitable.

The polyfunctional oligomers or polymers contain, above all, aliphatic or aromatic amino, hydroxyl, thiol or isocyanate and/or thioisocyanate groups. Suitable polyfunctional polymers are polyethyleneimine, polyvinyl alcohol, cellulose derivatives, polyvinylamine or polyvinylaniline; polyethyleneimine is preferred.

The membrane preferably contains sulfonic acid, carboxylic acid or ammonium groups as the ionic group. Membranes containing radicals of an anionic reactive dye are particularly advantageous.

Membranes consisting of a fundamental framework which contains polyacrylonitrile or a copolymer formed from acrylonitrile and other ethylenically unsaturated monomers are described, for example, in EP-A-25,973. The preparation of modified membranes of this type which can be employed in the process according to the invention is described in DE-A-3,035,134. The fundamental framework of the membrane is reacted with hydroxylamine (introduction of amidoxime groups into the membrane) and is then modified in the same manner as that described in the case of cellulose acetate membranes in EP-A-26,399.

The proportion of acrylonitrile units in the fundamental framework of the membrane is advantageously at least 5, and is preferably at least 20,

percent by weight. Copolymers of acrylonitrile and vinyl acetate, vinyl ethers, vinylpyridine, vinyl chloride, styrene, butadiene, (meth)acrylic acid, maleic anhydride, 2-aminomethylmethacrylate or allyl compounds or terpolymers or tetrapolymers based on acrylonitrile are preferred.

The membranes modified in this way can, if desired, also be subjected to a heat treatment (tempering). The effect of the heat treatment is substantially to determine the pore size of the membrane skin. The membrane is treated for 1 to 30 minutes at a temperature of 60 to 90°C, advantageously by dipping it into warm water. If desired, the compound containing ionisable groups are carried out (sic). Furthermore, the reaction can also be carried out before the polymeric material is processed to give the asymmetric membrane.

The membranes can have various shapes and can, for example, be in the form of discs, sheets, tubes, a bag, a cone or hollow fibres. In order to be able to employ them effectively for the separation of material, they must be integrated into appropriate systems (modules) and incorporated in equipment (for pressure permeation).

The pore size can be varied within the range indicated earlier in the text by graduated heat treatment. The average charge density (equal to the content of ionisable groups) of the membrane is advantageously 1 to 100 milli-equivalents per kg of dry membrane.

The solid preparations which are produced in accordance with the invention contain, as photoactivators, sulfonated zinc or aluminium phthalocyanines or mixtures thereof. Phthalocyanines which are preferred in this respect are sulfonated phthalocyanines of the formula



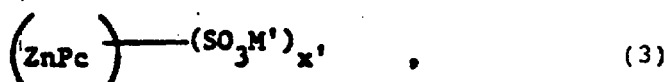
wherein MePc denotes the zinc or aluminium phthalocyanine ring system, M denotes hydrogen or an alkali metal ion or ammonium ion, R denotes fluorine, chlorine, bromine or iodine, x denotes any desired number from 1.3 to 4 and y denotes any desired number from 0 to 4, it being possible for

substituents R which are present in the molecule to be identical or different, or mixtures thereof.

The production of solid preparations of phthalocyanine photoactivators of the formula



wherein AlPc denotes the aluminium phthalocyanine ring system, M' denotes hydrogen, sodium or potassium, x' denotes any desired number from 2 to 4, R denotes fluorine, chlorine, bromine or iodine and y' denotes any desired number from 0 to 1.5, and also those of the formula



wherein ZnPc denotes the zinc phthalocyanine ring system, M' denotes hydrogen, sodium or potassium and X' denotes any desired number from 2 to 4 is of particular practical importance.

The sulfonated Al and Zn phthalocyanines are obtained from synthesis in the form of crude synthesis solutions or dispersions or as filter cakes or press cakes which contain, besides water, up to about 20% of organic by-products (starting materials, decomposition products and the like) and also up to 20% of inert salts (electrolytes). The latter originate mainly from the neutralisation and/or the salting out of the phthalocyaninesulfonate from the synthesis solution. These are, for example, alkali metal and alkaline earth metal salts, such as, for instance, ammonium chloride, sulfate or bisulfate, magnesium chloride, sulfate or bisulfate, sodium chloride, sulfate or bisulfate or potassium chloride, sulfate or bisulfate, above all sodium sulfate and especially sodium chloride. In order to carry out the first stage of the process according to the invention, the reaction mixture obtained direct from synthesis or an aqueous suspension of the moist filter cake or press cake mentioned above or of products which have already been dried is passed through the semi-permeable membrane in the manner described earlier in the text.

In the second stage of the process according to the invention, the concentrated aqueous photoactivator solution obtained after the passage through the membrane is subjected to gentle drying. This drying can be carried out in any desired known apparatus suitable for drying or granulating a solid substance from a liquid preparation. Examples of these are: nozzle atomisers, disc atomisers, crusher-driers, for example of the type "micron drier", or a fluidised bed unit. Freeze-drying is also possible. The drying can be carried out in batches or continuously. In the process according to the invention, the drying is preferably carried out in a granulating apparatus, for example by means of spray granulation, for instance in a nozzle atomiser equipped with a granulating attachment.

The solution obtained from the first stage (passage through the membrane) can be dried direct (without the addition of further substances). This gives a powder having a very high content of photoactivator and in other respects containing only residual moisture and very small amounts of inorganic salts (NaCl and Na_2SO_4) and organic byproducts from the synthesis. However, in order to improve the mechanical properties and especially to achieve a granulated commercial form, it is frequently advantageous to add, before the drying, extenders and/or surface-active substances, in particular those which are customary in the detergent industry and which are also suitable as constituents of detergents (washing powders). This has the advantage that when the photoactivators are incorporated into detergents (in particular if they are added to the slurry of washing powder), no extraneous substances are introduced which encumber the detergent and possibly have an unfavourable effect on it.

Examples of suitable extenders are alkali metal sulfates, carbonates, borates, phosphates, polyphosphates, bicarbonates and silicates, aminopolycarboxylates (such as, for example, Na ethylenediaminetetraacetate), phytates, polyphosphonates and polycarboxylates, carboxymethylcellulose, polysiloxanes or aluminium silicates in particular alkali metal chlorides, phosphates and sulfates, for example NaCl , Na_2HPO_4 , Na_3PO_4 and Na_2SO_4 , the latter being particularly preferred.

The surface-active substances can belong to the customary anionic,

nonionic, semipolar, ampholytic and/or zwitterionic classes of compounds. Examples of these are soaps, soluble salts of sulfonic acid half-esters of higher fatty alcohols, arylsulfonic acids containing higher and/or multiple alkyl substituents, sulfocarboxylic acid esters of medium to higher alcohols, fatty acid acylaminoalkylglycerolsulfonates or aminoarylglycerolsulfonates, phosphoric acid esters of fatty alcohols and the like, especially alkylbenzenesulfonates, alkylsulfates, ethoxylated alkyl ether-sulfates, paraffinsulfonates, α -olefinesulfonates, α -sulfocarboxylic acids and salts and esters thereof, alkyl glyceryl ether-sulfonates, fatty acid monoglyceridesulfates or monoglyceridesulfonates, alkylphenol polyethoxy ether-sulfates, 2-acyloxyalkanesulfonates, β -alkyloxyalkanesulfonates, soaps, ethoxylated fatty alcohols, alkylphenols, polypropoxyglycols, polypropoxyethylenediamines, amine oxides, phosphine oxides, sulfoxides, aliphatic secondary and tertiary amines, aliphatic quaternary ammonium, phosphonium and sulfonium (sic) compounds or mixtures of the said substances.

The resulting powders, or preferably granules, have a low dust content, that is to say they contain very few particles having a size less than 50 μm , or none. If necessary, small amounts of such particles can additionally be removed mechanically, for example by means of an air jet sieve. Preparations obtained in accordance with the invention have particle sizes within the range of 50-2000 μm , for example 60-1000 μm . In addition to the low dust content mentioned, they have a high mechanical strength (for example abrasion resistance), good stability on storage, low hygroscopicity, high bulk density and good solubility in cold water and wettability. The aqueous solutions of these preparations do not gel as do the solutions of the sulfonated zinc and aluminium phthalocyanine photoactivators prepared by known methods. In addition, mention should be made again of the extremely low content of interfering organic impurities (above all byproducts from the synthesis).

In a particularly preferred embodiment, sodium sulfate is added to the concentrated photoactivator solution obtained after passage through the membrane and the mixture is dried by spray granulation. Sufficient sodium sulfate is added so that the photoactivator granules obtained contain, for

example, 1 to 60, in particular 10 to 60, preferably 35 to 60, % by weight of Na_2SO_4 . Advantageously, that amount of Na_2SO_4 is added which corresponds to the amount of photoactivator present in the solution.

The photoactivator preparations obtained after addition of Na_2SO_4 by means of spray granulation are distinguished by a particularly good stability on storage and a low degree of water absorption. The granules thus obtained have particularly good free-flowing properties and have the advantages, listed above, of the preparations according to the invention to an especially high degree.

The solid photoactivator preparations obtained by the process according to the invention are themselves also a subject of the present invention. They contain, for example, 30-97% by weight of one or more sulfonated zinc and/or aluminium phthalocyanines, in particular those of the formula (1), 0-60% by weight of one or more extenders and/or surface-active substances which are customary in the detergent industry, 2 to 10% by weight of residual moisture, 0.05 to 1% by weight of NaCl and 0.1 to 2% by weight of organic byproducts.

Preferred photoactivator preparations contain 35 to 60% by weight of a sulfonated phthalocyanine of the formula (1), especially one of the formula (2) or (3), 35 to 60% by weight of Na_2SO_4 , 3 to 8% by weight of residual moisture, 0.1 to 0.5% by weight of NaCl, and 0.1 to 1% by weight of organic byproducts.

In the examples which follow, unless otherwise specified, parts denote parts by weight and percentages denote percentages by weight.

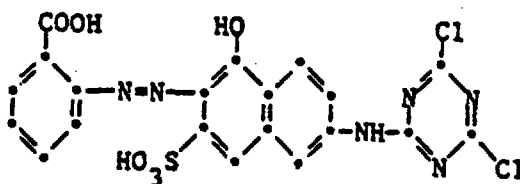
Examples of the preparation of preferred membranes which can be employed in the process according to the invention

A. In accordance with Example 1 of DE-A-2,505,524:

A solution is prepared from 25 g of cellulose acetate (degree of acetylation = 39.8%), 45 g of acetone and 30 g of formamide. It is allowed to

stand for 3 days and is poured onto a sheet of glass and spread with a spatula to give a layer 0.6 mm thick, the solvent is allowed to evaporate for 5 seconds at 25°C, the sheet of glass is placed in ice water for 2 hours and the resulting membrane is stripped off from the sheet of glass.

The membrane is then immersed in a 5% strength aqueous solution of the 1:2 chromium complex compound of the dye of the formula



and is left there for 48 hours at a pH of 6 and a temperature of 25°C. The pH of the dye solution is then adjusted to 10.4 by adding sodium hydroxide, and the solution is agitated continuously for 40 minutes at 25°C.

Instead of treating the membrane with the dye solution in two stages in this way, it can also be treated in one stage with a 10% strength solution of the chromium complex dye for 2 1/2 hours at a pH of 10.5 and at 25°C. The subsequent heat treatment (tempering) is carried out by placing the membrane in water at 60°C for 10 minutes.

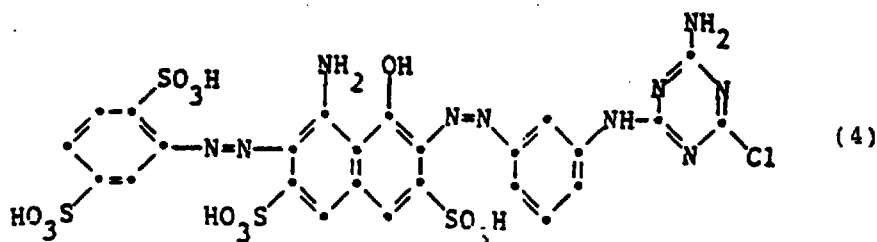
The preparation of further suitable membranes is described in the remaining examples of DE-A-2,505,254.

B. In accordance with Example 1 of DE-A-3,035,134:

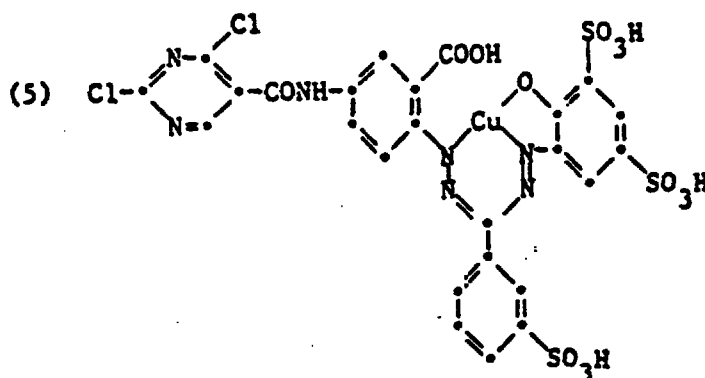
A membrane suitable for ultrafiltration, having a maximum pore diameter of 11.5 nm and composed of an 85:15 acrylonitrile/vinyl acetate copolymer (sic) having the following retention capacity:

2% strength sodium chloride solution	6%
1% strength sodium sulfate solution	10%
Dextrin (molecular weight 70,000)	60%
1% strength solution of the dye	
the formula (4)	34%

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is treated for 5 minutes at 65°C with an aqueous solution which contains 10% of hydroxylamine and 7.5% of sodium carbonate and has a pH of 6.5. The membrane is then removed from the solution and transferred to a stirred solution containing 370 mg of cyanuric chloride per 100 mg of membrane. This solution is kept at a pH of 10, for 30 minutes at 0°C by adding 1 N sodium hydroxide solution. The membrane is removed from this solution, washed with ice water and transferred to a stirred 10% strength solution of polyethyleneimine (molecular weight 40,000) and is kept there for 5 minutes at room temperature and at a pH of 10. The membrane is removed from this solution and is brought into contact with a solution containing 4% of the dye of the formula



and 10% of sodium chloride, and is kept in this solution for 15 minutes at room temperature. The membrane is then transferred to a 5% strength solution of sodium carbonate and kept there for 30 minutes at room temperature. After this treatment the flow and the retention capacity of the membrane for various dyes, salts and complexes are measured.

The preparation of further suitable membranes is described in the remaining examples of DE-A-3,035,134.

C. In accordance with Example 1 of EP-A-26,399:

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A cellulose acetate starting membrane (acetyl content 38.9%)
having the following specifications:

Molecular weight of dextrin, 95% of which is retained:	2000
Maximum working pressure:	13 bar
Pore diameter:	1.3 nm
Retention capacity for a 2% strength solution of the dye of the formula (4):	82 %
NaCl:	4.5%
Na ₂ SO ₄ :	15 %
Flow of a 2% strength solution of the dye of the formula (4):	55 litre/m ² .hr

is modified in the following manner: the membrane is treated for 15 minutes with a 5% strength solution of sodium bicarbonate and then, for 2 hours, with a 2% strength petroleum ether (boiling point 80-100°C) solution of cyanuric chloride. After the membrane thus treated has been rinsed in cold water, it is transferred to a 20% strength solution of polyethyleneimine (molecular weight 189), the pH of which has been adjusted to a value of 9 with sodium hydroxide, and is kept there for 2 hours at 40°C. The membrane is then rinsed with water for 2 hours. It is then immersed in a solution containing 5% of the reactive dye of the formula (5), 10% of sodium chloride and sufficient sodium carbonate to bring the pH to 10.5, and is left in this solution for 2 hours at room temperature. The retention capacity and the flow rate of the membrane is then tested.

The preparation of further suitable membranes is described in the remaining examples of EP-A-26,399.

Example 1:

The crude solution of ZnPc(SO₃Na)_{approx.4} (ZnPc = the zinc phthalocyanine ring system) which has been obtained from synthesis and has a solids content of about 13%, is passed through a modified cellulose acetate membrane (obtained, for example, in accordance with the above instructions A or C

for the preparation of membranes) having a membrane area of 0.25 m^2 , using an excess pressure of 25 bar, in a pilot plant for reverse osmosis, and is concentrated in this way for 6 hours, water being added in the amount of the initial volume. Sodium sulfate, in the amount of the photoactivator present in the solution, is added to the resulting photoactivator solution, which has a solids content of about 25%. The resulting mixture is dried in a nozzle atomiser fitted with a granulating nozzle to give granules which are then separated from particles $<60 \text{ }\mu\text{m}$ via a laboratory air jet sieve. A preparation of low dust content, high density and good abrasion resistance and having the following composition is obtained:

46.5% of $\text{ZnPc}(\text{SO}_3\text{Na})_{\text{approx.4}}$,
47.5% of Na_2SO_4 ,
0.15% of NaCl ,
0.85% of organic byproducts and
5 % of residual moisture.

The preparation has the properties listed in the table below. As a comparison, the values of a preparation produced in a customary manner (without purification and concentration through a semi-permeable membrane) have been included in the table.

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Table

Property or test method	Test value determined	
	Preparation according to the invention	Comparison preparation
Dust test	4	3
Hygroscopicity (water absorption under test conditions)	7.6% (free-flowing)	18.4% ("fused")
Abrasion resistance	4	2
Solubility at 60°C	85 g/litre	65 g/litre
Bulk density	0.63 kg/litre	0.48 kg/litre
Solubility in cold water	100 g/litre	64 g/litre
Suspension properties	readily wettable	moderately wettable
Particle size distribution (before sieving)		
< 60 µm	6%	18%
60-350 µm	74%	72%
> 350 µm	20%	10%
Stability on storage (3 months at room temperature)	-2.1%*)	-4.2%*)

*) Loss in activity

The performance and the assessment criteria of the tests listed in the table (dust test, abrasion resistance, solubility at 60°C, solubility in cold water, bulk density and suspension properties) are described in EP-A-37,382, pages 20-23.

It is also possible to employ a membrane according to preparation instruction B or any other membrane defined in the description.

Example 2:

A crude solution of $\text{AlPcCl}(\text{SO}_3\text{Na})_{3-4}$ (AlPc = the aluminium phthalocyanine ring system), obtained from synthesis, is purified and concentrated on a modified membrane by means of reverse osmosis in a manner analogous to that described in Example 1, and the product is spray-granulated. A solid preparation which is stable on storage and has a composition analogous to that indicated in Example 1, but having $\text{AlPcCl}(\text{SO}_3\text{Na})_{3-4}$ as the active substance instead of $\text{ZnPc}(\text{SO}_3\text{Na})_{\text{approx.}4}$ is obtained. The tests carried out on the resulting granules give results similar to those indicated in the table of Example 1.

The solid photoactivator preparations obtained by the process according to the invention can be processed further in a customary manner. For example they can be added in an appropriate amount, either as such or after being dissolved in water, to the slurry of a washing powder or to liquid detergent compositions.

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Patent Claims

1. Process for the preparation of solid photoactivator preparations containing sulfonated zinc and/or aluminium phthalocyanines as the photo-activators, characterised in that a crude solution containing the said photoactivators is passed through a semi-permeable, asymmetric membrane having a pore diameter of 0.1 to 50 nm which consists of a cellulose acetate fundamental framework modified by reaction with an ionic compound containing reactive groupings, or which consists of a fundamental framework which contains polyacrylonitrile or a copolymer formed from acrylonitrile and other ethylenically unsaturated monomers and which has been modified by reaction with hydroxylamine and subsequent reaction with a polyfunctional monomeric compound, a polyfunctional polymer and an ionic compound containing reactive groupings, and the resulting concentrated photoactivator solution is then dried under gentle conditions, it being possible to add, before drying, extenders and/or surface-active substances customary in the detergent industry.
2. Process according to Claim 1, characterised in that the membrane consists of a cellulose acetate fundamental framework which has been modified by reaction with a polyfunctional monomeric compound, a polyfunctional polymer and an ionic compound containing reactive groupings.
3. Process according to Claim 1 or 2, characterised in that the polyfunctional polymer in the fundamental framework of the membrane contains aliphatic or aromatic amino groups or hydroxyl, thiol, isocyanate and/or isothiocyanate groups.
4. Process according to Claim 3, characterised in that the polyfunctional polymer is derived from polyethyleneimine, polyvinyl alcohol, cellulose derivatives, polyvinylamine or polyvinylaniline.
5. Process according to Claim 1 or 2, characterised in that the membrane contains sulfonic acid, carboxylic acid or ammonium groups as the ionic groups.



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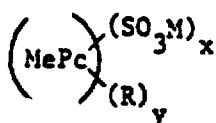
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6. Process according to Claim 1, characterised in that the membrane contains radicals of a water-soluble reactive dye as the ionic compound containing reactive groupings.

7. Process according to Claim 1, characterised in that the proportion of acrylonitrile units in the fundamental framework of the membrane is at least 5% and is preferably at least 20%.

8. Process according to Claim 7, characterised in that the fundamental framework of the membrane contains copolymers of acrylonitrile and vinyl acetate, vinyl ethers, vinylpyridine, vinyl chloride, styrene, butadiene, (meth) acrylic acid, maleic anhydride, 2-aminomethylmethacrylate or allyl compounds or terpolymers or tetrapolymers based on acrylonitrile.

9. Process according to Claim 1, characterised in that the sulfonated zinc or aluminium phthalocyanine employed is a phthalocyanine of the formula



wherein MePc denotes the zinc or aluminium phthalocyanine ring system, M denotes hydrogen or an alkali metal ion or ammonium ion, R denotes fluorine, chlorine, bromine or iodine, x denotes any desired number from 1.3 to 4 and y denotes any desired number from 0 to 4, it being possible for substituents R present in the molecule to be identical or different, or mixtures of such phthalocyanines.

10. Process according to one of Claims 1 to 9, characterised in that the concentrated aqueous photoactivator solution is dried in a granulating apparatus, preferably by means of spray granulation.

11. Process according to one of Claims 1 to 9, characterised in that the concentrated aqueous photoactivator solution is dried in an atomisation drier or in a fluidised bed unit.

12. Process according to one of Claims 1 to 11, characterised in that extenders and/or anionic, nonionic, semi-polar, ampholytic and/or



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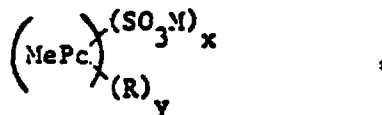
zwitterionic surface-active substances which are customary in the detergent industry are added to the concentrated aqueous photoactivator solution before it is dried.

13. Process according to Claim 12, characterised in that the extenders employed are alkali metal sulfates, carbonates, borates, phosphates, polyphosphates, bicarbonates and silicates, aminopolycarboxylates, phytates, polyphosphonates and polycarboxylates, carboxymethylcellulose, polysiloxanes or aluminium silicates, preferably sodium sulfate.

14. Process according to Claim 12, characterised in that the surface-active substances employed are alkylbenzenesulfonates, alkylsulfates, ethoxylated alkyl ether-sulfates, paraffinsulfonates, α -olefinesulfonates, α -sulfocarboxylic acids and salts and esters thereof, alkyl glyceryl ether-sulfonates, fatty acid monoglyceridesulfates or monoglyceridesulfonates, alkylphenol polyethoxy ether-sulfates, 2-acyloxyalkanesulfonates, β -alkyloxyalkanesulfonates, soaps, ethoxylated fatty alcohols, alkylphenols, polypropoxyglycols, polypropoxyethylenediamines, amine oxides, phosphine oxides, sulfoxides, aliphatic secondary and tertiary amines, aliphatic quaternary ammonium, phosphonium and sulfonium compounds or mixtures of the said substances.

15. Process according to Claim 13, characterised in that sodium sulfate is added prior to drying and the solution is dried by spray granulation.

16. Solid photoactivator preparation obtained in accordance with Claim 1, characterised in that it contains 30-97% by weight of one or more sulfonated zinc and/or aluminium phthalocyanines, in particular those of the formula



wherein MePc denotes the zinc or aluminium phthalocyanine ring system, M denotes hydrogen or an alkali metal ion or ammonium ion, R denotes fluorine, chlorine, bromine or iodine, x denotes any desired number from 1.3 to 4 and y denotes any desired number from 0 to 4, it being possible for



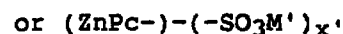
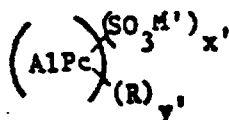
substituents R present in the molecule to be identical or different, 0-60% by weight of one or more extenders and/or surface-active substances which are customary in the detergent industry, 2 to 10% by weight of residual moisture, 0.05 to 1% by weight of NaCl and 0.1 to 2% by weight of organic byproducts.

17. Preparation according to Claim 16, characterised in that it contains, as extenders, alkali metal sulfates, carbonates, borates, phosphates, polyphosphates, bicarbonates and silicates, aminopolycarboxylates, phytates, polyphosphonates and polycarboxylates, carboxymethylcellulose, polysiloxanes or aluminium silicates, preferably sodium sulfate.

18. Preparation according to Claim 16, characterised in that it contains, as surface-active substances, alkylbenzenesulfonates, alkyl sulfates, ethoxylated alkyl ether-sulfates, paraffinsulfonates, α -olefinesulfonates, α -sulfocarboxylic acids and salts and esters thereof, alkyl glyceryl ethersulfonates, fatty acid monoglyceride sulfates or monoglyceride sulfonates, alkylphenol polyethoxy ether sulfates, 2-acyloxyalkane sulfonates, β -alkyloxyalkane sulfonates, soaps, ethoxylated fatty alcohols, alkylphenols, polypropoxyglycols, polypropoxyethylenediamines, amine oxides, phosphine oxides, sulfoxides, aliphatic secondary and tertiary amines, aliphatic quaternary ammonium, phosphonium and sulfonium compounds or mixtures of the said substances.

19. Preparation according to Claim 16, characterised in that it contains 35 to 60% by weight of a phthalocyanine photoactivator of the formula indicated in Claim 16, 35 to 60% by weight of Na_2SO_4 , 3 to 8% by weight of residual moisture, 0.1 to 0.5% by weight of NaCl, and 0.1 to 1% by weight of organic byproducts.

20. Preparation according to one of Claims 16-19, characterised in that it contains, as the sulfonated phthalocyanine, a phthalocyanine of the formula



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wherein AlPc denotes the aluminium phthalocyanine ring system, ZnPc denotes the zinc phthalocyanine ring system, M' denotes hydrogen, sodium or potassium, x' denotes any desired number from 2 to 4, R denotes fluorine, chlorine, bromine or iodine and y' denotes any desired number from 0 to 1.5.

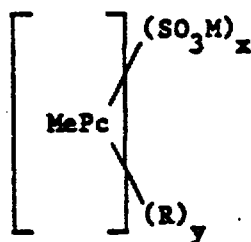


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- as for the preparation of a solid photoactivator formulation containing sulfonated zinc and/or phthalocyanines as photoactivators, which comprises passing a crude solution containing said photoactivators through a semipermeable asymmetrical membrane having a pore diameter of 0.1 to 50 nm and consisting of a cellulose acetate basic structure which is modified by reaction with an ionic compound which contains reactive groups, or which consists of a basic structure which contains polyacrylonitrile or a copolymer of acrylonitrile and other ethylenically unsaturated monomers, and which is modified by reaction with polyethyleneimine and subsequent reaction with a polyfunctional monomer, a polyfunctional polymer and an ionic compound which contains reactive groups, and subsequently drying the concentrated photoactivator solution obtained under mild conditions and, if desired, adding fillers and/or surfactants customarily employed in the detergent industry before drying said solution.
2. A process according to claim 1, wherein the membrane consists of a cellulose acetate basic structure which is modified by reaction with a polyfunctional monomer, a polyfunctional polymer and an ionic compound which contains reactive groups.
 3. A process according to either of claims 1 or 2, wherein the polyfunctional polymer in the basic structure of the membrane contains aliphatic or aromatic amino groups, hydroxyl, thiol, isocyanate and/or isothiocyanate groups.
 4. A process according to claim 3, wherein the polyfunctional polymer is derived from polyethyleneimine, polyvinyl alcohol, cellulose derivatives, polyvinylamine or polyvinylaniline.
 5. A process according to either of claims 1 or 2, wherein the membrane contains sulfonic acid, carboxylic acid or ammonium groups as ionic groups.
 6. A process according to claim 1, wherein the membrane contains radicals of a water-soluble reactive dye as ionic compound which contains reactive groups.
 7. A process according to claim 1, wherein the basic structure of the membrane contains at least 5 %, and preferably at least 20%, of acrylonitrile units.
 8. A process according to claim 7, wherein the basic structure of the membrane contains copolymers of acrylonitrile and vinyl acetate, vinyl ethers, vinyl pyridine, vinyl chloride, styrene, butadiene, acrylic or methacrylic acid, maleic anhydride, 2-aminomethylmethacrylate or allyl compounds or terpolymers or tetrapolymers of acrylonitrile.
 9. A process according to claim 1, which comprises the use of a sulfonated zinc or aluminium phthalocyanine of the formula



- wherein MePc is the zinc or aluminium phthalocyanine ring system, M is hydrogen, an alkali metal ion or an ammonium ion, R is fluorine, chlorine, bromine or iodine, x is any value from 1.3 to 4 and y is any value from 0 to 4, with the proviso that substituents R in the molecule may be identical or different, or a mixture thereof.
10. A process according to any one of claims 1 to 9, wherein the concentrated aqueous photoactivator solution is dried in a granulator, preferably by spray granulation.
 11. A process according to any one of claims 1 to 9, wherein the concentrated aqueous photoactivator solution is dried in a spray drier or in a fluid bed drier.
 12. A process according to any one of claims 1 to 11, wherein fillers and/or anionic, nonionic, semipolar, ampholytic and/or zwitterionic surfactants customarily used in the detergent industry are added to the concentrated aqueous photoactivator solution before drying said solution.



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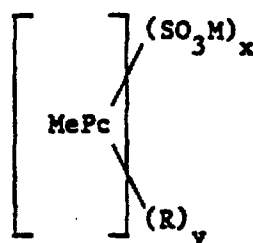
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According to claim 12, wherein the fillers employed are alkali metal sulfates, carbonates, borates, polyphosphates, bicarbonates and silicates, aminopolycarboxylates, phytates, phosphonates and polycarboxylates, carboxymethyl cellulose, polysiloxanes or aluminium silicates, as fillers.

According to claim 12, wherein the surfactants employed are alkylbenzenesulfonates, ethoxylated alkyl ether sulfates, paraffin sulfonates, α -olefin sulfonates, α -sulfocarboxylic acids and esters thereof, alkyl glyceryl ether sulfonates, fatty acid monoglyceride sulfates or sulfonates, polyethoxy ether sulfates, 2-acyloxyalkane sulfonates, β -alkyloxyalkane sulfonates, soaps, ethoxylated fatty alcohols, alkylphenols, polypropoxy glycols, polypropoxyethylenediamines, amine oxides, phosphine oxides, sulfoxides, aliphatic secondary and tertiary amines, aliphatic quaternary ammonium, phosphonium and sulfonium compounds, or mixtures of the above surfactants.

According to claim 13, wherein sodium sulfate is added before drying and the solution is dried by granulation.

A solid photoactivator formulation obtained according to the process as claimed in claim 1, which formulation contains 30 to 97 % by weight of a sulfonated aluminium and/or zinc phthalocyanine, in particular the formula



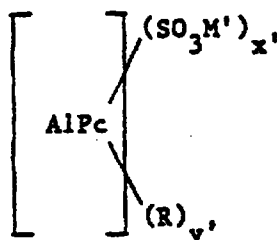
wherein MePc is the zinc or aluminium phthalocyanine ring system, M is hydrogen, an alkali metal ion or an ammonium ion, R is fluorine, chlorine, bromine or iodine, x is any value from 1.3 to 4 and y is any value from 0 to 4, with the proviso that substituents R in the molecule may be identical or different, 0 to 60 % by weight of one or more fillers and/or surfactants customarily employed in the detergent industry, 2 to 10 % by weight of residual moisture, 0.05 to 1 % by weight of NaCl, and 0.1 to 2 % by weight of organic by-products.

17. A formulation according to claim 16, which contains alkali metal sulfates, carbonates, borates, phosphates, polyphosphates, bicarbonates and silicates, aminopolycarboxylates, phytates, polyphosphonates and polycarboxylates, carboxymethyl cellulose, polysiloxanes or aluminium silicates, preferably sodium sulfate, as fillers.

18. A formulation according to claim 16, which contains alkylbenzenesulfonates, alkylsulfates, ethoxylated alkyl ether sulfates, paraffin sulfonates, α -olefin sulfonates, α -sulfocarboxylic acids and salts and esters thereof, alkyl glyceryl ether sulfonates, fatty acid monoglyceride sulfates or sulfonates, alkylphenol polyethoxy ether sulfates, 2-acyloxyalkane sulfonates, β -alkyloxyalkane sulfonates, soaps, ethoxylated fatty alcohols, alkylphenols, polypropoxy glycols, polypropoxyethylenediamines, amine oxides, phosphine oxides, sulfoxides, aliphatic secondary and tertiary amines, aliphatic quaternary ammonium, phosphonium and sulfonium compounds, or mixtures of the above surfactants as surfactants.

19. A formulation according to claim 16, which contains 35 to 60 % by weight of a phthalocyanine photoactivator of the formula as indicated in claim 16, 35 to 60 % by weight of Na_2SO_4 , 3 to 8 % by weight of residual moisture 0.1 to 0.5 % by weight of NaCl and 0.1 to 1 % by weight of organic by-products.

20. A formulation according to any one of claims 16 to 19, which contains a sulfonated phthalocyanine of the formula



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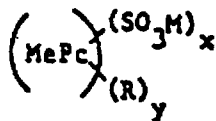
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b)-(SO₃M')_x

rein AlPc is the aluminium phthalocyanine ring system, ZnPc is the zinc phthalocyanine ring system, M' is hydrogen, sodium or potassium, x' is any value from 2 to 4, R is fluorine, chlorine, bromine or iodine and y' is any value from 0 to 1.5.

revendications

1. Procédé pour la préparation de compositions solides de photoactivateurs, contenant en tant que photo-activateurs des zinco- et/ou aluminophthalocyanines sulfonées, caractérisé par le fait que l'on fait passer une solution brute, contenant les photoactivateurs cités, sur une membrane semi-perméable, asymétrique, présentant un diamètre de pores de 0,1 à 50 nm, qui est constituée d'un réseau de base d'acétate de cellulose qui est modifié par réaction avec un composé ionique comportant des groupements réactifs, ou qui est constituée d'un réseau de base qui contient du polyacrylonitrile ou un copolymère d'acrylonitrile et d'autres monomères à insaturation éthylénique, lequel réseau est modifié par réaction avec de l'hydroxylamine et réaction subséquente avec un composé monomère polyfonctionnel, un polymère polyfonctionnel et un composé ionique comportant des groupements réactifs, et ensuite on sèche de façon ménagée la solution concentrée de photo-activateur ainsi obtenue, des adjuvants et/ou des substances tensio-actives, utilisés habituellement dans l'industrie des détergents, pouvant être ajoutés avant le séchage.
2. Procédé selon la revendication 1, caractérisé par le fait que la membrane est constituée d'un réseau de base d'acétate de cellulose qui est modifié par réaction avec un composé monomère polyfonctionnel, un polymère polyfonctionnel et un composé ionique comportant des groupements réactifs.
3. Procédé selon la revendication 1 ou 2, caractérisé par le fait que le polymère polyfonctionnel présent dans le réseau de base de la membrane comporte des groupes amino, hydroxyle, thiol, isocyanate, et/ou isothiocyante, aliphatiques ou aromatiques.
4. Procédé selon la revendication 3, caractérisé par le fait que le polymère polyfonctionnel dérive de la polyéthylène-imine, du poly(alcool vinylique), de dérivés de la cellulose, de la polyvinylamine ou de la polyvinylaniline.
5. Procédé selon la revendication 1 ou 2, caractérisé par le fait que la membrane contient en tant que groupes ioniques des groupes sulfo, carboxyle ou ammonium.
6. Procédé selon la revendication 1, caractérisé par le fait que la membrane contient, en tant que composé ionique-comportant des groupements réactifs, des restes d'un colorant réactif soluble dans l'eau.
7. Procédé selon la revendication 1, caractérisé par le fait que la proportion des motifs acrylonitrile dans le réseau de base de la membrane s'élève au moins à 5% et, de préférence, au moins à 20%.
8. Procédé selon la revendication 7, caractérisé par le fait que le réseau de base de la membrane contient des copolymères d'acrylonitrile et d'acétate de vinyle, d'éthers vinyliques, de vinylpyridine, de chlorure de vinyle, de styrène, de butadiène, d'acide (méth)acrylique, d'anhydride maléique, de 2-aminométhyl-acrylate le méthyle ou de composés allyle, ou bien des ter- ou tétrapolymères à base d'acrylonitrile.
9. Procédé selon la revendication 1, caractérisé par le fait que l'on utilise en tant que zinco- ou aluminophthalocyanine une telle phthalocyanine de formule



dans laquelle MePc représente le système cyclique zinco- ou aluminophthalocyanine; M représente un atome d'hydrogène, un ion alcalin ou ammonium; R représente le fluor, le chlore, le brome ou l'iode; x est un nombre quelconque allant de 1,3 à 4; et y est un nombre quelconque allant de 0 à 4; les substituants R présents dans la molécule pouvant être identiques ou différents; ou des mélanges de telles phthalocyanines.

10. Procédé selon l'une des revendications 1 à 9, caractérisé par le fait que l'on sèche la solution aqueuse concentrée de photo-activateur dans un appareil de granulation, de préférence au moyen d'une granulation par pulvérisation.

11. Procédé selon l'une des revendications 1 à 9, caractérisé par le fait que l'on sèche la solution aqueuse concentrée de photo-activateur dans un sécheur-atomiseur ou dans une installation tourbillonnaire.

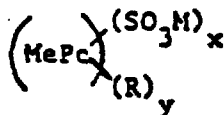
12. Procédé selon l'une des revendications 1 à 11, caractérisé par le fait qu'avant le séchage on ajoute à la solution aqueuse concentrée de photo-activateur des adjuvants et/ou des substances tensio-actives anioniques, non ioniques, semi-polaires, ampholytes et/ou amphotères, utilisés habituellement dans l'industrie des détergents.



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- procédé selon la revendication 12, caractérisé par le fait que l'on utilise en tant qu'adjuvants des sulfates, des borates, phosphates, polyphosphates, bicarbonates et silicates, de métaux alcalins, des polycarboxylates, des phytates, des polyphosphonates et polycarboxylates, la carboxyméthylcellulose, des siloxanes ou des silicates d'aluminium, de préférence le sulfate de sodium.
- procédé selon la revendication 12, caractérisé par le fait que l'on utilise en tant que substances tensio-actives des benzènesulfonates d'alkyle, des sulfates d'alkyle, des alkyléthersulfates oxyéthylés, des sulfonates de paraffine, des sulfonates d' α -oléfines, des acides α -sulfocarboxyliques, leurs sels et leurs esters, des glycéryléthersulfonates, des sulfates ou des sulfonates de monoglycérides d'acides gras, des alkylphénol-polyéthoxyéthersulfates, des 2-acyloxyalcane-sulfonates, des β -alkyloxyalcane-sulfonates, des savons, des alcools gras oxy-éthylés, des alkylphénols, des polypropoxyglycols, des polypropoxy-éthylènediamines, des oxydes d'amines, des oxydes de phosphines, des sulfoxydes, des amines aliphatiques secondaires ou tertiaires, des composés ammonium, phosphonium ou sulfonium quaternaire aliphatiques, ou des mélanges des substances citées.
15. Procédé selon la revendication 13, caractérisé par le fait que l'on ajoute du sulfate de sodium avant le séchage et que l'on sèche la solution par granulation par pulvérisation.
16. Composition solide de photo-activateur obtenue selon la revendication 1, caractérisée par le fait qu'elle contient de 30 à 97% en poids d'une ou de plusieurs zinco- et/ou alumino-phthalocyanines sulfonées, en particulier de formule



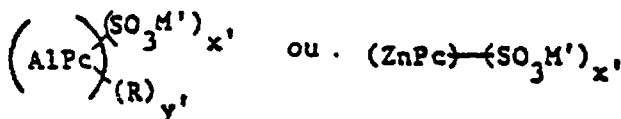
dans laquelle MePc représente le système cyclique zinco- ou aluminophthalocyanine; M représente un atome d'hydrogène ou un ion alcalin ou ammonium R représente le fluor, le chlore, le brome ou l'iode, x est un nombre quelconque allant de 1,3 à 4, et y est un nombre quelconque allant de 0 à 4, les substituants R présents dans la molécule pouvant être identiques ou différents; 0-60% en poids d'un ou de plusieurs adjuvants et/ou une ou plusieurs substances tensio-actives utilisés habituellement dans l'industrie des détergents; de 2 à 10% en poids d'humidité résiduelle; de 0,05 à 1% en poids de NaCl; et de 0,1 à 2% en poids de sous-produits organiques.

17. Composition selon la revendication 16, caractérisée par le fait qu'elle contient en tant qu'adjuvants des sulfates, carbonates, borates, phosphates, polyphosphates, bicarbonates et silicates, de métaux alcalins, des aminopolycarboxylates, des phytates, des polyphosphonates et polycarboxylates, de la carboxyméthylcellulose, des polysiloxanes ou des silicates d'aluminium, de préférence du sulfate de sodium.

18. Composition selon la revendication 16, caractérisée par le fait qu'elle contient en tant que substances tensio-actives des benzènesulfonates d'alkyle, des sulfates d'alkyle, des alkyléthersulfates oxyéthylés, des sulfonates de paraffine, des sulfonates d' α -oléfines, des acides α -sulfocarboxyliques, leurs sels et leurs esters, des alkylglycéryléthersulfonates, des sulfates ou des sulfonates de monoglycérides d'acides gras, des alkylphénol-polyéthoxyéthersulfates, des 2-acyloxyalcane-sulfonates, des β -alkyloxyalcane-sulfonates, des savons, des alcools gras oxy-éthylés, des alkylphénols, des polypropoxyglycols, des polypropoxy-éthylènediamines, des oxydes d'amines, des oxydes de phosphines, des sulfoxydes, des amines aliphatiques secondaires ou tertiaires, des composés ammonium, phosphonium ou sulfonium quaternaire aliphatiques, ou des mélanges des substances citées.

19. Composition selon la revendication 16, caractérisée par le fait qu'elle contient de 35 à 60% en poids d'un photo-activateur de type phthalocyanine de formule indiquée dans la revendication 16, de 35 à 60% en poids de Na_2SO_4 , de 3 à 8% en poids d'humidité résiduelle, de 0,1 à 0,5% en poids de NaCl et de 0,1 à 1% en poids de sous-produits organiques.

20. Composition selon l'une des revendications 16 à 19, caractérisée par le fait qu'elle contient en tant que phthalocyanine sulfonée une phthalocyanine de formule



dans lesquelles AlPc représente le système cyclique aluminophthalocyanine, ZnPc représente le système cyclique zincophthalocyanine, M' représente un atome d'hydrogène, de sodium ou de potassium, x' est un nombre quelconque allant de 2 à 4, R représente le fluor, le chlore, le brome ou l'iode, et y est un nombre quelconque allant de 0 à 1,5.

