

24

Description

The present invention relates to a process for preventing the gelation of concentrated aqueous solutions of photoactivators containing, as the photoactivators, sulfonated zinc phthalocyanines and/or aluminium phthalocyanines, and to the non-gelling, concentrated aqueous solutions thus obtained, which are stable on storage.

Sulfonated zinc and aluminium phthalocyanines are known as excellent photoactivators which are mainly used as photo-bleaching agents and, in some cases, 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 various detergents.

Hitherto great difficulties have been encountered in preparing usable commercial forms of the said photoactivators. The phthalocyaninesulfonates are obtained in a relatively impure state from synthesis. As a rule they contain up to 30 % of organic and inorganic by-products. The latter are mainly salts, such as NaCl and Na₂SO₄. The amount of organic by-products present is, for example, up to 15 %, in the form of a large number of compounds, some of which have not been identified. These by-products are extremely undesirable since they could, for example, adversely affect the action of the photoactivator. Attempts have been made to remove these by-products by chemical means. The results have, however, not given complete satisfaction. The aqueous solutions obtained in this manner have still contained an excessive amount of by-products, 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 consisted in the fact 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 being scarcely pourable any more. This problem has been encountered particularly in the case of sulfonated aluminium phthalocyanine.

25

It was therefore the object of the present invention to find a means of preparing a liquid, aqueous commercial form of the said photoactivators which does not have the disadvantages listed above. In particular, it was the object of the present invention to find a process by means of which the gelation of the liquid, aqueous commercial form could be prevented or at least reduced. Furthermore, the latter should have as high as possible a concentration of photoactivator, be stable on storage for a long time and contain as little as possible in the way of organic impurities and inorganic salts.

It has been found, surprisingly, that the objects mentioned above can be achieved by passing a crude solution of the photoactivators through a specific semi-permeable, asymmetric membrane when the photoactivator solutions are prepared.

Membrane separation processes are known, for example, from DE-A-2,204,725, 2,805,891 and 2,948,292. EP-A-59,782 describes a process for the production of aqueous dyestuff preparations, particularly preparations containing reactive dyestuffs, by means of a membrane separation process in which formulation auxiliaries are added, if appropriate, to the formulations.

In none of the publications mentioned is it described or suggested that it is possible, by means of the process according to the invention, to obtain non-gelling photoactivator solutions which, surprisingly, contain extremely little in the way of by-products (compared with the dyestuff solutions of the state of the art) and which, also surprisingly, have a substantially better stability on storage.

The process according to the invention for preventing the gelation of concentrated aqueous photoactivator solutions containing sulfonated zinc and/or aluminium phthalocyanines consists in passing a crude solution containing the said photoactivators, in order to prepare concentrated solutions containing less than 1 % by weight of NaCl and Na₂SO₄, 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.

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 and sodium acetate, or low-molecular impurities, for example unreacted or partially decomposed starting materials. They are, however, also intended to be able to separate differently charged ions.

The retention or separation (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 with a diameter of 0.1 to 50 nm. 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 allow water and dissolved substances which, by virtue of their molecular sizes, are below the separation 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 per cent or more, without loss of

22

photoactivator, in a single filtration passage. In the course of this the volume of the solution of retained substances (on 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, expediently to its initial volume. 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 of cellulose acetate or polyacrylonitrile or a copolymer of acrylonitrile and other ethylenically unsaturated monomers 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 dyestuffs which can belong to various categories, such as anthraquinone, azo or formazan dyestuffs. 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 permit these reagents to be attached to the starting polymers: carboxylic acid halide groups, sulfonic acid halide groups, radicals of α,β -unsaturated carboxylic acids or amides, for example acrylic, methacrylic, α -chloroacrylic or α -bromoacrylic acid, 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 vinylsulfonyl groups or carboxyvinyl groups; radicals containing the

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, dihalogenopyridazines, 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, 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 dyestuffs) containing sulfonic acid, carboxylic acid or ammonium groups are preferred.

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

Membranes composed of (partially acetylated) cellulose acetate can, for example, be modified directly by reaction with the reactive ionic compounds mentioned above, in particular anionic reactive dyestuffs (cf., for example, German Offenlegungsschrift 2,505,254).

A further modification of cellulose acetate can [lacuna], for example, by 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 dyestuff, 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 dyestuff are particularly advantageous.

Membranes consisting of a fundamental framework containing polyacrylonitrile or a copolymer formed from acrylonitrile and other ethylenically unsaturated monomers are described, for example, in European Published Patent Application 25,973. The preparation of modified membranes of this type which can be employed in the process according to the invention is described in German Offenlegungsschrift 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 is described in the case of cellulose acetate membranes in European Published Patent Application 26,399.

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

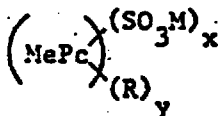
The membranes thus modified can, if required, also be subjected to a heat

treatment ("tempering"). The effect of the heat treatment is to determine substantially the size of the pores 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 heat treatment can also be carried out before the reaction with the reactive compound containing ionisable groups. 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 be in the form of, for example, a disc, a sheet, a tube, a bag, a cone or hollow fibres. In order to enable them to be employed effectively for the separation of material, they must be integrated into appropriate systems (modules) and incorporated into 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.

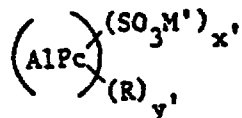
The aqueous solutions which are prepared in accordance with the invention contain, as photoactivators, sulfonated zinc or aluminium phthalocyanines or mixtures thereof. Sulfonated phthalocyanines which are preferred in this respect are those of the formula



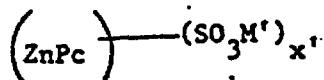
wherein MePc denotes the zinc or aluminium phthalocyanine ring system, M denotes hydrogen, an alkali metal ion or ammonium ion, R denotes fluorine, chlorine, bromine or iodine, x denotes any desired number from 1.3 to 4 and y denotes any desired number from 0 to 4, it being possible for the substituents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

The preparation of concentrated, non-gelling liquid formulations of

phthalocyanine photoactivators of the formula



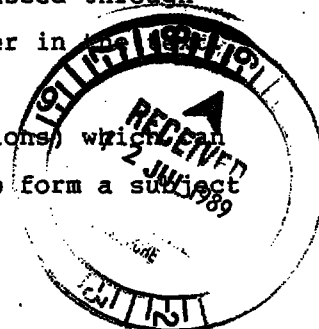
wherein AlPc denotes the aluminium phthalocyanine ring system, M' denotes hydrogen, sodium or potassium, x' denotes any desired number from 2 to 4, R denotes fluorine, chlorine, bromine or iodine and y' denotes any desired number from 0 to 1.5, and also those of the formula (SO M')[sic]



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 in the form of filter cakes or press cakes containing, 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 process according to the invention, the reaction mixture obtained directly from the synthesis or an aqueous suspension of the moist filter cake or press cake mentioned above or of the product which has already been dried is passed through the semi-permeable membrane in the manner described earlier in

The aqueous solutions of photoactivators (liquid formulations) which can be obtained by the process according to the invention also form a subject



32

of the present invention. They contain extremely low proportions of organic and inorganic impurities and have a high concentration of photo-activator. They are excellently stable on storage and do not gel, even when stored for a long time.

Non-gelling, concentrated, aqueous photoactivator solutions (photo-activator formulations) according to the invention, which are stable on storage, contain, for example, 5-50 % by weight of one or more sulfonated aluminium and/or zinc phthalocyanines, particularly those of the formula (1), 0.05 to 1 % by weight of neutral salts, especially NaCl and Na₂SO₄, and 0.05 to 2 % by weight of organic by-products.

Preferred photoactivator solutions according to the invention contain 10 to 35 % by weight of a sulfonated phthalocyanine of the formula (1) and especially of the formula (2) or (3), 0.01 to 0.2 % by weight of NaCl, 0.1 to 0.8 ...[sic] of Na₂SO₄ and 0.1 to 1 % of organic by-products.

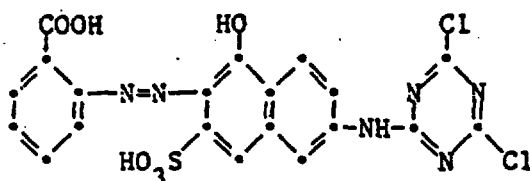
In the examples which follow, unless otherwise specified, parts denote parts by weight and percentages denote percentages by weight.

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 German Offenlegungsschrift 2,505,254:

A solution is prepared from 25 g of cellulose acetate (degree of acetylation = 39.8 %), 45 g of acetone and 30 g of formamide. This solution is allowed to stand for three days and is poured onto a sheet of glass and spread by means of 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 dyestuff 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 dyestuff solution is then brought to 10.4 by adding sodium hydroxide, and the solution is agitated continuously for 40 minutes at 25°C.

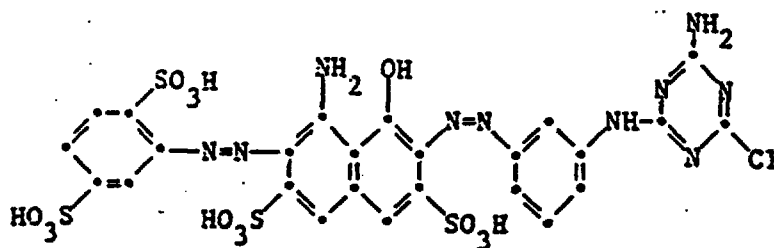
Instead of treating the membrane with the dyestuff solution in two stages in this way, it is also possible to treat it in one stage for 2 1/2 hours with a 10% strength solution of the chromium complex dyestuff, at pH 10.5 and at 25°C. The subsequent heat treatment (tempering) is carried out by placing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

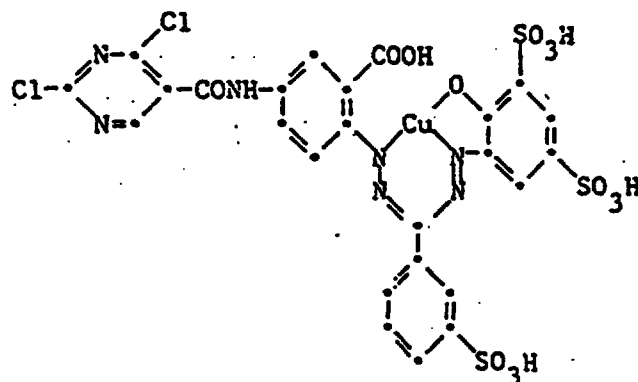
B. In accordance with Example 1 of DE-A-3,035,134:

A membrane suitable for ultrafiltration, having a maximum pore diameter of 11.5 nm, composed of an 85:15 acrylonitrile/vinyl acetate copolymer which has 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 dyestuff of the formula (4)	34%



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 put into a stirred solution containing 370 mg of cyanuric chloride per 100 g 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 put into a stirred 10% strength solution of polyethyleneimine (molecular weight 40,000) and kept there for 5 minutes at room temperature and at a pH of 10. The membrane is removed from this solution and brought into contact with a solution containing 4 % of the dyestuff 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 retention capacity of the membrane for various dyestuffs, salts and complexes is measured.

The preparation of further suitable membranes is described in the remaining examples of German Offenlegungsschrift 3,035,134.

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

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 dyestuff of the formula (4): 82 %
NaCl: 4.5 %
Na₂SO₄: 15 %
Flow of a 2% strength solution of the
dyestuff of the formula (4): 55 L/m-h [sic]

is modified in the following way: the membrane is treated for 15 minutes with a 5% strength solution of sodium bicarbonate and is then treated for 2 hours with a 2% strength petroleum ether (boiling point 80-100°C) solution of cyanuric chloride. After the membrane treated in this way has been rinsed in cold water, it is put into a 20% strength solution of polyethyleneimine (molecular weight 189) which has been adjusted to a pH of 9 with sodium hydroxide, and is kept there for 2 hours at 40°C. The membrane is then washed with water for 2 hours. It is then immersed in a solution containing 5% of the reactive dyestuff 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 are then tested.

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

Example 1: A crude solution, obtained from synthesis, of ZnPc(SO₃Na) approx. 4 [sic] (ZnPc = the zinc phthalocyanine ring system), which 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 surface of 0.25²m [sic], using 25 bar of excess pressure, in a pilot plant for reverse osmosis, and is thus concentrated for 6 hours, water being added in the same amount as the initial volume. A concentrated photoactivator solution containing, in addition to water

36

24.6 % of $\text{ZnPc}(\text{SO}_3\text{Na})_{\text{approx. } 4}$,

< 0.1 % of NaCl

0.3 % of Na_2SO_4 and

0.4 % of organic by-products

is obtained. The photoactivator solution obtained by the process according to the invention is thus virtually free from interfering impurities.

The resulting solution (liquid formulation) is excellently stable on storage and does not gel even if left to stand for a long time.

It is also possible to employ a membrane according to the instructions for preparation B above 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 by means of reverse osmosis on a modified membrane in a manner analogous to that described in Example 1. A concentrated, non-gelling formulation of $\text{AlPcCl}(\text{SO}_3\text{Na})_{3-4}$ is obtained which is excellently stable on storage and contains amounts of by-products similar to those indicated in Example 1.

Liquid formulations obtained by the process according to the invention can be processed further in the customary manner. For example, they can be added in an appropriate amount, if appropriate after dilution with water, to the slurry of a washing powder or to liquid detergent compositions.



37

Patent Claims

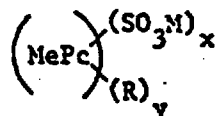
1. Process for preventing the gelation of concentrated aqueous photo-activator solutions containing sulfonated zinc and/or aluminium phthalocyanines, characterised in that, in order to prepare concentrated solutions containing less than 0.1 % by weight of NaCl and Na₂SO₄, a crude solution containing the said photoactivators is passed through a semi-permeable, asymmetric membrane having a pore diameter of 1 [sic] to 500 [sic] 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.
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 [sic] groups or hydroxyl, thiol, isocyanate and/or isothiocyanate groups.
4. Process according to claim 3, characterised in that the polyfunctional polymer is polyethyleneimine, polyvinyl alcohol, a cellulose derivative, polyvinylamine or polyvinylaniline.
5. Process according to claim 1 or 2, characterised in that the membrane contains, as the ionic groups, sulfonic acid, carboxylic acid or ammonium groups.
6. Process according to claim 1, characterised in that the membrane

contains, as the ionic compound containing reactive groupings, radicals of a water-soluble reactive dyestuff.

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%.

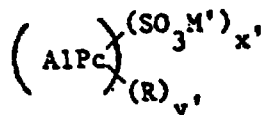
8. Process according to claim 7, characterised in that the fundamental framework of the membrane contains copolymers of acrylonitrile and vinyl acetate, vinyl ethers, vinylpyridine, vinyl chloride, styrene, butadiene, (meth)acrylic acid, maleic anhydride, 2-aminomethylmethacrylate or allyl compounds 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, 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 the substituents R present in the molecule to be identical or different, or mixtures of such phthalocyanines.

10. Process according to claim 9, characterised in that the phthalocyanine employed is a phthalocyanine of the formula

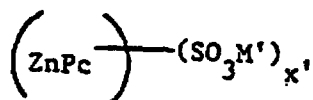


wherein AlPc denotes the aluminium phthalocyanine ring system, M' denotes hydrogen, sodium or potassium, x' denotes any desired number from 2 to 4, R denotes fluorine, chlorine, bromine or iodine and y' denotes any

29

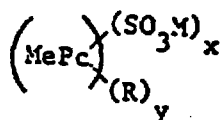
desired number from 0 to 1.5.

11. Process according to claim 9, characterised in that the phthalocyanine employed is a phthalocyanine 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.

12. Non-gelling, concentrated, aqueous photoactivator solution which is stable on storage and is obtained in accordance with claim 1, characterised in that it contains 5 to 50 % by weight of one or more sulfonated aluminium and/or zinc phthalocyanines, in particular of the formula

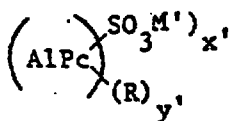


wherein MePc denotes the zinc or aluminium phthalocyanine ring system, M denotes hydrogen, an alkali metal ion or ammonium ion, R denotes fluorine, chlorine, bromine or iodine, x denotes any desired number from 1.3 to 4 and y denotes any desired number from 0 to 4, it being possible for substituents R present in the molecule to be identical or different, 0.05 to 1 % by weight of neutral salts, in particular NaCl and Na₂SO₄, and 0.05 to 2 % by weight of organic by-products.

13. Solution according to claim 12, characterised in that it contains 10 to 35 % by weight of a phthalocyanine photoactivator of the formula indicated in claim 12, 0.01 to 0.2 % by weight of NaCl, 0.1 to 0.8 % by weight of Na₂SO₄ and 0.1 to 1 % by weight of organic by-products.

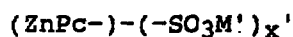
14. Solution according to claim 12, characterised in that it contains, as the phthalocyanine, a phthalocyanine of the formula

40



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.

15. Solution according to claim 12, characterised in that it contains, as the phthalocyanine, a phthalocyanine 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.



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Claims

1. A process for preventing the gelation of concentrated aqueous photoactivator solutions containing sulfonated zinc and/or aluminium phthalocyanines, which process comprises, in order to prepare concentrated solutions containing less than 1 % by weight of NaCl and Na₂SO₄, passing a crude measurable asymmetrical membrane having a pore diameter of 0.1 to and consisting of a cellulose acetate basic structure which is modified by reaction with an ionic compound which contains polyacrylonitrile or a copolymer of acrylonitrile and other ethylenically unsaturated monomers, and which is modified by reaction with hydroxylamine and subsequent reaction with a polyfunctional monomer, a polyfunctional polymer and an ionic compound which contains reactive groups.

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 membrane basic structure 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 polyethyleneimine, polyvinyl alcohol, a cellulose derivative, polyvinylamine or polyvinylaniline.

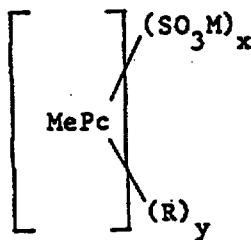
5. A process according to either of claims 1 or 2, wherein the membrane contains sulfonic acid, carboxylic acid or ammonium groups as ionic groups.

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



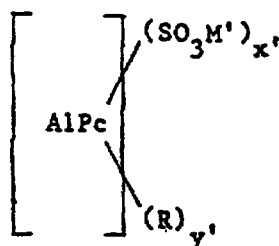
wherein MePc is the zinc or aluminium phthalocyanine ring system, M is hydrogen, an alkali metal ion or an ammonium ion, R is fluorine, chlorine, bromine or iodine, x is any value from 1.3 to 4 and y is any value from 0 to 4, with the proviso that substituents R in the molecule may be identical or different, or a mixture thereof.

10. A process according to claim 9, which comprises the use of a phthalocyanine of the formula



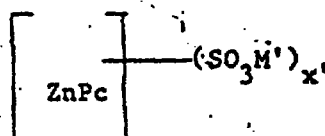
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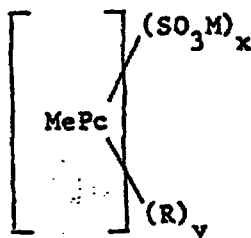
wherein AlPc is the aluminium phthalocyanine ring system, M' is hydrogen, sodium or potassium x' is any value from 2 to 4, R is fluorine, chlorine, bromine or iodine and y' is any value from 0 to 1.5.

11. A process according to claim 9, which comprises the use of a phthalocyanine of the formula



wherein ZnPc is the zinc phthalocyanine ring system, M' is hydrogen, sodium or potassium, and x' is any value from 2 to 4.

12. A non-gelling, concentrated, storage-stable aqueous photoactivator solution obtained according to the process as claimed in claim 1, which solution contains 5 to 50% by weight of one or more sulfonated aluminium and/or zinc phthalocyanines, in particular of the formula



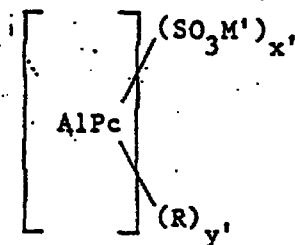
wherein MePc is the zinc or aluminium phthalocyanine ring system, M is hydrogen, an alkali metal ion or an ammonium ion, R is fluorine, chlorine, bromine or iodine, x is any value from 1.3 to 4 and y is any value from 0 to 4, with the proviso that substituents R in the molecule may be identical or different 0.05 to 1 % by weight of neutral salts, in particular NaCl and Na₂SO₄, and 0.05 to 2 % by weight of organic by-products.

13. A solution according to claim 12, which contains 10 to 35% by weight of a phthalocyanine photoactivator of the formula as indicated in claim 12, 0.01 to 0.2 % by weight of NaCl, 0.1 to 0.8 % by weight of Na₂SO₄ and 0.1 to 1 % by weight of organic by-products.



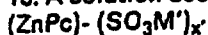
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14. A solution according to claim 12, which contains a phthalocyanine of the formula



wherein AlPc is the aluminium 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.

15. A solution according to claim 12, which contains a phthalocyanine of the formula



wherein ZnPc is the zinc phthalocyanine ring system, M' is hydrogen, sodium or potassium, and x' is any value from 2 to 4.

Revendications

1. Procédé pour empêcher la gélification de solutions aqueuses concentrées de photo-activateurs, contenant des zinco- et/ou aluminophthalocyanines sulfonées, caractérisé par le fait que, pour la préparation de solutions concentrées contenant moins de 1% en poids de NaCl et de Na₂SO₄, 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.

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 isothiocyanate; aliphatiques ou aromatiques.

4. Procédé selon la revendication 3, caractérisé par le fait que le polymère polyfonctionnel est la polyéthylène-imine, le poly(alcool vinylique), un dérivé de la cellulose, la polyvinylamine ou la polyvinylaniline.

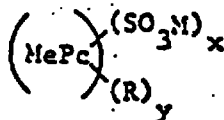
5. Procédé selon la revendication 1 ou 2, caractérisé par le fait que la membrane contient en tant que groupes ioniques des groupes sulfo, carboxyle ou ammonium.

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 de 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

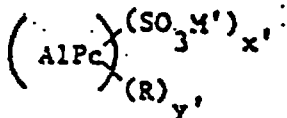


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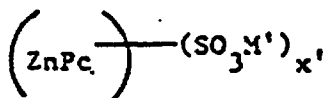
nombre quelconque allant de 1,3 à 4; et y est un nombre quelconque allant de 0 à 4; les substituants R présents dans la molécule pouvant être identiques ou différents; ou des mélanges de telles phthalocyanines.

10. Procédé selon la revendication 9, caractérisé par le fait que l'on utilise en tant que phthalocyanine une phthalocyanine de formule



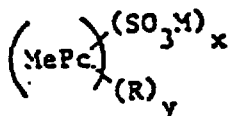
dans laquelle AlPc représente le système cyclique alumino-phthalocyanine; M' représente un atome d'hydrogène, de sodium ou de potassium; x' est un nombre quelconque allant de 2 à 4; R représente le fluor, le chlore, le brome ou l'iode; et y' est un nombre quelconque allant de 0 à 1,5.

11. Procédé selon la revendication 9, caractérisé par le fait que l'on utilise en tant que phthalocyanine une phthalocyanine de formule



dans laquelle ZnPc représente le système cyclique zinco-phthalocyanine; M' représente un atome d'hydrogène, de sodium ou de potassium; et x' est un nombre quelconque allant de 2 à 4.

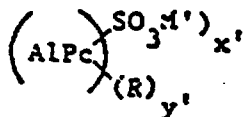
12. Solution aqueuse de photo-activateur, ne se gélifiant pas, concentrée, stable au stockage, obtenue selon la revendication 1, caractérisée par le fait qu'elle contient de 5 à 50% en poids d'une ou plusieurs alumino-et/ou zinco-phthalocyanines sulfonées, en particulier de formule



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; 0,05 à 1% en poids de sels neutres, en particulier NaCl et Na₂SO₄, et 0,05 à 2% en poids de sous-produits organiques.

13. Solution selon la revendication 12, caractérisée par le fait qu'elle contient de 10 à 35% en poids d'un photo-activateur de type phthalocyanine de formule indiquée dans la revendication 12, de 0,01 à 0,2% en poids de NaCl, de 0,1 à 0,8% en poids de Na₂SO₄ et 0,1 à 1% en poids de sous-produits organiques.

14. Solution selon la revendication 12, caractérisée par le fait qu'elle contient en tant que phthalocyanine une phthalocyanine de formule



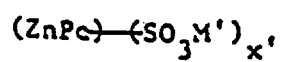
dans laquelle AlPc représente le système cyclique alumino-phthalocyanine; M' représente un atome d'hydrogène, de sodium ou de potassium; x' est un nombre quelconque allant de 2 à 4; R représente le fluor, le chlore, le brome ou l'iode; et y' est un nombre quelconque allant de 0 à 1,5.

15. Solution selon la revendication 12, caractérisée par le fait qu'elle contient en tant que phthalocyanine une phthalocyanine de formule



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dans laquelle ZnPc représente le système cyclique zinco-phthalocyanine; M' représente un atome d'hydrogène, de sodium ou de potassium; et x' est un nombre quelconque allant de 2 à 4.