

[54] DETERGENTS
[75] Inventors: Frank Lohmann, Arlesheim,
Switzerland; Claude Eckhardt,
Mulhouse, France; Karl Kleiber,
Arlesheim, Switzerland
[73] Assignee: Ciba-Geigy AG, Basel, Switzerland
[22] Filed: June 19, 1972
[21] Appl. No.: 263,901

3,573,211	3/1971	Zweidler et al.....	252/95
3,627,758	12/1971	Weber et al.....	252/95 XR
3,640,874	2/1972	Gray	252/95
3,646,015	2/1972	Hamilton	252/95
3,681,248	8/1972	Gould et al.....	252/89
3,706,670	12/1972	Gray	252/95

Primary Examiner—Mayer Weinblatt
Attorney, Agent, or Firm—Joseph G. Kolodny; Edw.
McC. Roberts; Prabodh I. Almaula

[30] Foreign Application Priority Data
June 25, 1971 Switzerland..... 9353/71
[52] U.S. Cl..... 252/95, 117/33.5 R, 252/89,
252/316
[51] Int. Cl..... C11d 7/54
[58] Field of Search..... 252/95, 89, 316;
117/33.5 R

[56] References Cited
UNITED STATES PATENTS
3,401,123 9/1968 Brynko et al. 252/316

[57] ABSTRACT
The present invention provides dry, free-flowing de-
tergents which contain chlorine donors and a fluo-
rescent whitener the particles of which are encased by a
water-soluble coating agent.
The encased fluorescent whiteners have a greatly
enhanced stability during the storage life of the
detergent.

10 Claims, No Drawings

1 DETERGENTS

The use of detergent compositions and of washing liquors which contain chlorine donors is gaining increasing importance, in particular for washing procedures at low temperatures. Since most detergents contain fluorescent whiteners, or the washing procedures are carried out in the presence of fluorescent whiteners, it is essential that these whitening agents are sufficiently stable towards such chlorine donors.

In order to simplify the washing procedure, these chlorine donors are being incorporated to an increasing degree into the detergent in the form of compounds which are stable when dry and only split off chlorine in the washing liquor. In a large number of fluorescent whiteners, especially those containing water-solubilising groups, it has been observed that these compounds become at least partially decomposed when the detergent is stored, despite the fact that they are sufficiently stable to chlorine in the washing liquor. Besides the stability to chlorine of fluorescent whiteners in the washing liquor, an additional requisite for their incorporation into detergents which contain chlorine donors is that they must be stable in the said detergents during the storage life of these latter.

From German Offenlegungsschrift 1.926.084 it is known to protect fluorescent whiteners from the detergent components by incorporating them in particles which effervesce in water. These effervescent particles must be admixed dry with the detergent; however, this proves disadvantageous in achieving a uniform distribution of the fluorescent whitener in small concentrations.

It is also already known to coat water-insoluble fluorescent whiteners with film-forming organic protective substances in order to prevent them from agglomerating over long periods of storage. Compared with this known procedure, the present invention is based on the quite different problem of protecting water-soluble fluorescent whiteners from attack by chlorine donors while retaining the direct incorporation of the fluorescent whitener into the detergent slurry.

The discovery has been made that it is possible to protect certain groups of fluorescent whiteners, namely those from the series of the distyryl-diphenyls and styrylnaphthotriazoles, from attack by chlorine donors if their particles are coated with a water-soluble polymer. Carboxyalkyl celluloses, chiefly carboxymethyl cellulose, have proved particularly suitable for this purpose. In so doing, it was particularly surprising that it is possible to protect water-soluble fluorescent whiteners with a water-soluble polymer quite adequately, even on adding the fluorescent whitener to the aqueous slurry.

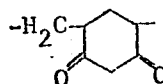
Besides the preferred substances cited hereinbefore, it is also possible in principle to use other organic, water-soluble polymeric substances as coating agents, primarily those which liberate the coated fluorescent whitener on introducing it into an aqueous alkaline medium within at most about 5 minutes, but preferably within about 2 minutes. During this process the weight ratio between fluorescent whitener and protective substances may be between 9:1 and 1:99; but in general it is between 4:1 and 1:4, preferably between 2:1 and 1:2.

Suitable substances of this kind are described e.g. in "Water Soluble Resins," by R. L. Davidson and Marshall Siftig, Reinhold Publ. Corp., New York, 1962.

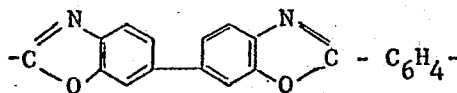
2

As examples there may be cited:

Polyvinyl pyrrolidones, water-soluble polymers containing carboxyl groups, such as polyacrylic and methacrylic acid, copolymers which contain maleic acid or maleic anhydride, such as methylvinyl ether-maleic acid, ethylene maleic acid, styrene-maleic acid copolymers of acetic acid vinyl ester and crotonic acid, also water-soluble salts of these polymeric acids, likewise water-soluble half esters and their salts, polyacrylamide, polyvinyl alcohol, water-soluble starch or sugar, shellac, casein, polysulphone resins, polymers with structural elements of the formula



water-soluble urea/formaldehyde and melamine/formaldehyde condensation products, poly-[3,3'-methylimino-bis-trimethyleneadipic amide], polybenzoxazoles with structural elements of the formula



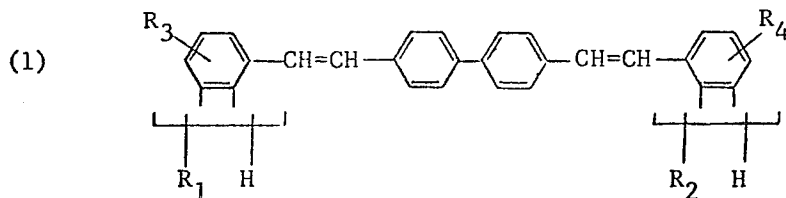
cellulose sulphate ester, polyvinyl piperidone, gelatin, pectin, heparin, alginic acid and its salts, polystyrenesulphonic acid, cyanoethyl cellulose, hydroxyalkyl cellulose.

Of industrial interest are coating agents from the group of the polyvinyl pyrrolidones, polymers of acrylic and methacrylic acid and their esters and amide derivatives, styrene-maleic copolymers, polyvinyl alcohols, water-soluble starches, water-soluble urea/formaldehyde and melamine/formaldehyde condensation products, cellulose sulphate esters, carboxyalkyl cellulose, alginic acid and salts.

Preferred coating agents are, as already mentioned, carboxyalkyl celluloses, such as carboxymethyl cellulose; also suitable are hydroxyethyl celluloses and polyvinyl alcohol. The term "hydroxyalkyl cellulose" is to be understood as meaning here in addition to the hydroxyalkyl cellulose in the narrow sense, e.g. hydroxypropyl cellulose or hydroxyethylhydroxypropyl cellulose, also the alkylhydroxyalkyl cellulose, i.e., those cellulose ethers in which not all etherically bonded alkyl radicals contain hydroxyl groups, where they are water-soluble, thus, for example, water-soluble ethylhydroxyethyl celluloses, methylhydroxyethyl celluloses or methylhydroxypropyl celluloses. (Included in the term "water-soluble" are also substances which form colloidal aqueous solutions).

The coating agents may be applied to the fluorescent whiteners singly or in admixture. In addition, they may contain additives, e.g. ionogenic or non-ionogenic dispersing agents or plasticisers.

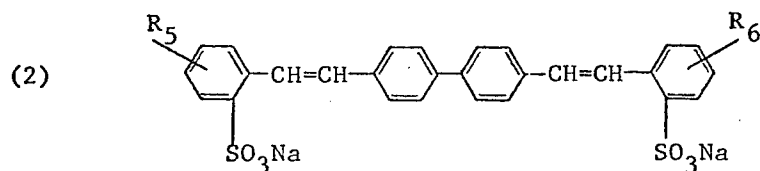
Suitable fluorescent whiteners for the incorporation into the detergents according to the invention are: I. Bis-stilbene compounds of the formula



wherein R_1 represents a sulfo group or the salts thereof, R_2 represents hydrogen, chlorine, methyl, methoxy or a sulfo group or the salts thereof, R_3 and R_4 independently represent hydrogen, chlorine, methyl or methoxy. Preferred compounds are those of the formula

As active detergents it is possible to use anionic, cationic, amphoteric and non-ionogenic surfactants or mixtures of these surfactants. Anionic surfactants are preferred.

The anionic surfactants comprise soaps and other carboxylates, derivatives of sulphur-oxyacids or phosphorus-oxyacids, as well as compounds which contain nitrogen in the hydrophilic group.

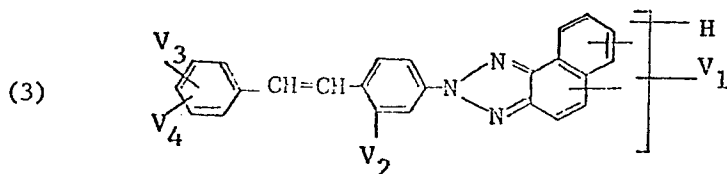


wherein R_5 and R_6 independently represent hydrogen, chlorine, methyl or methoxy.

phorus-oxyacids, as well as compounds which contain nitrogen in the hydrophilic group.

Water-soluble salts of higher fatty and resinic acids may be cited as examples of soaps.

II. Stilbynaphthotriazoles of the formula



wherein V_1 represents hydrogen or a sulfo group or the salts thereof, V_2 represents hydrogen, chlorine, a cyano group, a carboxyl group or a sulfo group or the salts thereof, V_3 represents hydrogen, methoxy or a sulfo group or the salts thereof, and V_4 represents hydrogen or chlorine, with at least one of the substituents V_1 to V_4 representing a sulfo group or the salts thereof.

In addition to the fluorescent whitener sealed within the coating agent the preparations according to the invention contain the conventional detergent constituents. Besides the active detergents (surfactants) it is possible to add e.g. builders, bleaching agents and special additives, such as wetting agents (e.g., polywaxes and polyglycols for increasing the soil suspending power), superfatting agents, fungicides and deodorants, also filler and the like.

As dry chlorine donors which release hypochlorite ions on contact with water importance attaches primarily to heterocyclic N-chloroimides, such as trichloroisocyanuric acid and dichloroisocyanuric acid and the salts thereof, e.g. sodium or potassium trichloroisocyanurate. However, it is also possible to use other imides, e.g. N-chlorosuccinimide, N-chlorophthalimide, 1,3-dichloro-5,5-dimethylhydantoin etc., as well as other compounds which split off hypochlorite, e.g. trichloromelamine or N,N-dichlorobenzoylene-urea. It is, of course, also possible to use inorganic salts of hypochlorous acid, such as lithium or calcium hypochlorite.

Derivatives of sulphur-oxyacids are mostly sulphates, such as sulphates of higher alcohols or sulphonates, e.g. alkylbenzenesulphonates and olefin sulphonates.

Preferred derivatives of phosphorus-oxyacids are phosphates, whereas e.g. disulphimide salts exemplify the type which contains nitrogen in the hydrophilic groups.

The cationic surfactants comprise amines and their salts, for example N-2-aminoethylstearylamine or N-2-aminoethylstearylamine, benzyl-dimethyl-stearyl-ammonium chloride, trimethyl-cetyl-ammonium bromide, etc., also onium compounds and amino oxides.

Amphoteric surfactants contain basic and acid hydrophilic groups in the same molecule. As examples of amphoteric surfactants there may be cited N-alkyl-β-aminopropionic acids or N-alkyl, N,N-dimethylglycines whose alkyl radicals contains 8 to 24 carbon atoms.

The non-ionogenic surfactants comprise polyhydroxy compounds, surfactants based on mono- or polysaccharides, higher molecular acetylene glycols and substituted polyglycol ethers with the particularly important ethylene oxide adducts, for example isooctylphenol, with about 8 to 30 ethylene oxide units.

Phosphates, in particular condensed phosphates, silicates, borates, carbonates and organic builders, for example the salts of nitrilotriacetic acid or ethylene-diamine-tetraacetic acid may be used as water-soluble builders. In general, 0.5 to 10 parts of bi-

ulder are used to one part of surfactant (active detergent).

The detergents according to the invention are used chiefly for washing cotton fabrics. But they may also be used with advantage for cleansing textiles made from other cellulose fibres, such as rayon, or other fibres, such as synthetic polyamides, e.g., silk, wool, polyester, cellulose acetates, polyacrylonitrile, or mixtures of two or more of these types of fibre, e.g., cottonpolyester fibre fabrics.

As already mentioned, the stabilisation of the fluorescent whitener(s) is attained by coating it (or them) with one of the substances cited hereinbefore. This coating is carried out by dissolving or dispersing the fluorescent whitener in an aqueous solution of the coating agent and then evaporating this solution to dryness, for example by the spray drying process. In this way there is first of all obtained a storable dry preparation which may then at any desired time be further processed to manufacture the detergents according to the invention.

To incorporate the fluorescent whitener into the detergent the procedure generally is that the fluorescent whitener obtained in the manner described hereinbefore is distributed as uniformly as possible in the slurry which, except for the chlorine donor and optionally perborate, contains all the constituents of the detergent. The amount of fluorescent whitener to be pasted into the slurry is generally so fixed that the detergent according to the invention contains 0.01 to 2, preferably 0.05 to 1 percent by weight thereof. The detergent slurry is then dried, for example once more by spray drying. The end product is obtained by admixing the chlorine donor and optionally perborate with the thus obtained dry preparation.

Example 1

A sodium carboxymethyl cellulose (62.5 g) with a low viscosity and an etherification degree of 0.8 is dissolved in 750 g of water. Then the sodium salt of 4,4'-bis-(2-sulphostyryl)-diphenyl (62.5 g) is added to the solution. This mixture is homogenised and spray dried. The resulting dry preparation (4g) is then pasted into a slurry containing 150 g of dodecylbenzenesulphonate, 100 g of sodium lauryl sulphonate, 400 g of sodium tripolyphosphate, 255 g of calcined sodium sulphate, 70 g of sodium metasilicate (9 hydrate), 20 g of carboxymethyl cellulose and 5 g of ethylenediamine-tetraacetic acid, and this mixture is then dried at 90°C. The resulting product is granulated and then mixed with 50 g of trichloroisocyanurate.

Samples of the thus manufactured product are tested for their whitening action after 1, 7 and 30 days storage at room temperature.

The comparison is made with detergent samples of the above described composition which have likewise been stored for 1, 7 and 30 days and on the one hand contain trichloroisocyanurate and on the other contain no trichloroisocyanurate, but into which the fluorescent whitener has been introduced without protective coating.

In addition to these comparative tests, cotton samples are washed for 15 minutes at 40°C in washing liquors each containing 4 g of detergent/l at a liquor

ratio of 1:20, the detergent having been added exactly 1 minute before the cotton was introduced. The degree of whiteness of the washed samples is determined by the "Ciba Whiteness Scala" (cf. Journal of the Soc. Dyers and Col. 84, 1968, 125-132). The results are given in the following Table.

Table 1

Detergent Sample	Degree of whiteness of cotton samples after washing with detergent stored for days		
	1	7	30
detergent containing trichloroisocyanurate and FWA = fluorescent whitener treated with CMC	205	200	197.5
detergent containing trichloroisocyanurate and untreated FWA	197.5	160	145
detergent with FWA	227.5	227.5	227.5

Similar results are obtained by using 4,4'-bis-(2-sulpho-5-chloro-styryl)-diphenyl or its sodium salt instead of 4,4'-bis-(2-sulphostyryl)-diphenyl.

Example 2

The process as described in Example 1 is carried out, except that 37.5 g of FWA is treated with 87.5 g of sodium carboxymethyl cellulose (CMC) and of this preparation 6.7 g is pasted into the detergent slurry. The results are given in the following Table.

Table II

Detergent Sample	Degree of whiteness of cotton samples after washing with detergent stored for days		
	1	7	30
detergent containing trichloroisocyanurate and FWA treated with CMC	200	180	180
detergent containing trichloroisocyanurate and untreated FWA	197.5	157.5	142.5

Example 3

The process as described in Example 1 is carried out, except that 87.5 g of FWA is treated with 37.5 g of CMC and 2.9 g of this preparation is pasted into the detergent slurry. The results are given in the following Table.

Table III

Detergent Sample	Degree of whiteness of cotton samples after washing with detergent stored for days		
	1	7	30
detergent containing trichloroisocyanurate and FWA treated with CMC	200	195	190
detergent containing trichloroisocyanurate and untreated FWA	197.5	157.5	142.5

7

Example 4

The process described in Example 1 is carried out, except that the sodium salt of 4-[naphtho-1',2':4,5-triazolyl-(2)]-2-sulpho-stilbene is used as FWA and polyvinyl alcohol (Gohsenol GL 03) is used as coating agent and the fabric is washed at 50°C. The results are given in the following Table.

Table IV

Detergent Sample	Degree of whiteness of cotton samples after washing with detergent stored for days		
	1	7	30
detergent containing tri-chloroisocyanurate and FWA treated with polyvinyl alcohol	190	175	165
detergent containing tri-chloroisocyanurate and untreated FWA	190	155	127.5
detergent with FWA	195	195	195

Example 5

The process described in Example 1 is carried out, except that the sodium salt of 4-[naphtho-1',2':4,5-triazolyl-(2)]-2-sulphostilbene is used as FWA and polyvinyl alcohol (Gohsenol GL 03) is used as coating agent and polyamide samples (Bodanyl-Helanca) are washed with the detergent samples at 30°C. The results are given in the following Table 5.

Table 5

Detergent Sample	Degree of whiteness of polyamide samples after washing with detergent stored for days		
	1	7	30
detergent containing tri-chloroisocyanurate and FWA treated with polyvinyl alcohol	182.5	167.5	145
detergent containing tri-chloroisocyanurate and untreated FWA	192.5	145	125
detergent with FWA	197.5	197.5	197.5

Example 6

The process described in Example 1 is carried out, except that the sodium salt of 4-(2-sulphostyryl)-4'-(2-chlorostyryl)-diphenyl is used as FWA and polyvinyl alcohol (Gohsenol GL 03), is used as coating agent and the fabric is washed at 50°C. The results are given in the following Table.

Table VI

Detergent Sample	Degree of whiteness of cotton samples after washing with detergent stored for days		
	1	7	30
detergent containing tri-chloroisocyanurate and FWA treated with polyvinyl alcohol	200	198.5	145
detergent containing tri-chloroisocyanurate and untreated FWA	195	145	130
detergent with FWA	215	215	215

8

Example 7

The process described in Example 1 is carried out, except that the sodium salt of 4-(2-sulphostyryl)-4'-(2-chlorostyryl)-diphenyl is used as FWA and polyvinyl alcohol (Gohsenol GL 03) is used as coating agent and the polyamide samples (Bodanyl-Helanca) are washed with the detergent samples at 30°C. The results are given in Table VII.

Table VII

Detergent Sample	Degree of whiteness of polyamide samples washed with detergent stored for days		
	1	7	30
detergent containing tri-chloroisocyanurate and FWA treated with polyvinyl alcohol	187.5	167.5	152.5
detergent containing tri-chloroisocyanurate and untreated FWA	197.5	135	122.5
detergent with FWA	212.5	212.5	212.5

Example 8

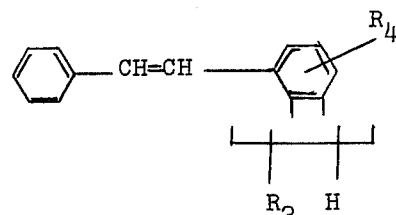
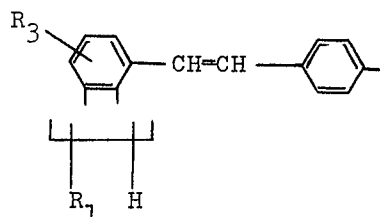
The process described in Example 1 is carried out, except that 50 g of FWA is treated with 75 g of hydroxycellulose (Klucel E) and 5 g of this product is pasted into the detergent slurry and the washing tests are carried out after 2 hours, 3 and 12 days. The results are given in the following Table.

Table VIII

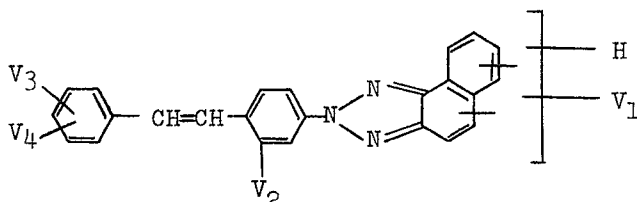
Detergent Sample	Degree of whiteness of cotton samples after washing with detergent stored for		
	2 hrs.	3 days	12 days
detergent containing tri-chloroisocyanurate and FWA treated with hydroxyethyl cellulose	197.5	175	167.5
detergent containing tri-chloroisocyanurate and untreated FWA	182.5	135	127.5
detergent with FWA	225	225	225

We claim:

1. Dry, free-flowing detergent compositions consisting essentially of a surfactant, a chlorine donor which releases hypochlorite ions on contact with water and a fluorescent whitener selected from the group consisting of a distyryldiphenyl whitener of the formula



wherein R_1 represents a sulpho group or the salts thereof, R_2 represents hydrogen, chlorine, methyl, methoxy or a sulpho group or the salts thereof, R_3 and R_4 independently represent hydrogen, chlorine, methyl or methoxy and a stilbylnaphthotriazole whitener of the formula



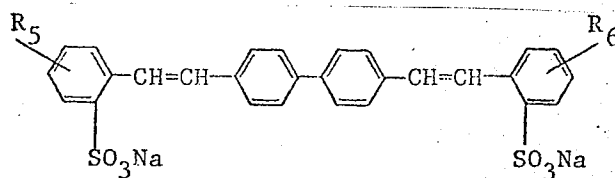
wherein V_1 represents hydrogen or a sulpho group, or the salts thereof, V_2 represents hydrogen, chlorine, a cyano group, a carboxyl group, or a sulpho group or the

4. Detergent compositions according to claim 1, wherein the fluorescent whitener particles contain carboxymethyl cellulose, hydroxypropyl cellulose or polyvinyl alcohol as water-soluble organic coating agent.

5. Detergent compositions according to claim 1, wherein the weight ratio between fluorescent whitener

and coating agent is 4:1 to 1:4.

6. Detergent compositions according to claim 1, which contain fluorescent whiteners of the formula



salts thereof, V_3 represents hydrogen, methoxy or a sulpho group or the salts thereof, and V_4 represents hydrogen or chlorine, with at least one of the substituents V_1 to V_4 standing for a sulpho group or the salts thereof, the particles of which are encased by a watersoluble or organic coating agent, the weight ratio between said fluorescent whitener and said water-soluble organic protecting agent being between 9:1 and 1:99.

2. Dry, free-flowing detergent compositions according to claim 1, which contain an anionic surfactant as active detergent, chlorine donors, and a fluorescent whitener from the series of the distyryldiphenyls and stilbylnaphthotriazoles which contains at least one sulpho group (or the salts thereof) and the particles of which are encased by a water-soluble coating agent.

3. Detergent compositions according to claim 1, wherein the fluorescent whitener particles contain carboxymethyl cellulose as water-soluble organic coating agent.

wherein R_5 and R_6 independently represent hydrogen, chlorine, methyl or methoxy.

7. Detergent compositions according to claim 1, which contain 4-[naphtho-1',2':4,5-triazolyl-(2)]-2-sulphostilbene as fluorescent whitener.

8. Detergent compositions according to claim 6, which contain 4,4'-bis-(2-sulphostyryl)-diphenyl as fluorescent whitener.

9. Detergents according to claim 6, which contain 4-(2-sulphostyryl)-4'-(2-chlorostyryl)-diphenyl as fluorescent whitener.

10. A process for the manufacture of products of the composition cited in claim 1, wherein a solution or dispersion of the fluorescent whitener in an aqueous solution of the coating agent is evaporated to dryness, the resulting dry preparation pasted into the detergent slurry which is then evaporated, and the resulting product is optionally granulated and the chlorine donor mixed therewith.

* * * * *

50

55

60

65