

UNITED STATES PATENT OFFICE

2,673,186

ALKALINE DETERGENT COMPOSITION

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4 Claims. (Cl. 252—132)

1

This invention relates to detergent products having alkaline reaction and containing whitening (or color brightening) agents of a fluorescent nature.

Coumarin derivatives, particularly beta methyl umbelliferone (4-methyl-7-hydroxycoumarin), have found a variety of uses which take advantage of their abilities to absorb ultraviolet radiations and to emit fluorescent radiations in the blue end of the visible spectrum, and which are in part dependent also on the color-free character of many of these derivatives when viewed in visible light which is free from ultraviolet radiations. Such compounds are used, for instance, as ultraviolet filters in photography, in suntan lotions, and in transparent wrappers for perishable foods, as "optical bleaches" to improve the whiteness of paper and textiles, as whitening agents in off-white soaps and other substances, and as color brightening agents in a variety of products.

The present invention is concerned with the incorporation of a selected group of coumarin derivatives as whitening or brightening agents in compositions having at least a mildly alkaline nature, and particularly in substances of this character which are processed—after the addition of the fluorescent material—at elevated temperatures. Among such compositions are ordinary soaps (alkali metal salts of the higher fatty acids), washing compounds containing such soaps, and washing compounds containing both synthetic organic detergents and alkaline inorganic salts such as alkaline phosphates, polyphosphates, carbonates, silicates, and borates. The manufacture of detergent compositions of this character frequently includes mixing and/or otherwise processing the ingredients while in molten condition at temperatures which may range from about 140° F. to as high as 450° F., sometimes in the presence of small amounts of free sodium hydroxide which is, as a rule, subsequently neutralized.

The term "synthetic organic detergent," as used herein, includes within its meaning all of the non-soap anionic detergents which are characterized by their high solubility in water, their resistance to precipitation by the constituents of hard water, and their surface active and effective detergent properties, such as water-soluble salts of sulfuric and phosphoric reaction products of alkyl and substituted alkyl compounds containing from 8 to 18 carbon atoms in the alkyl group; and all of the non-ionic detergents which are similarly characterized by high solubility in

2

water, resistance to precipitation by the constituents of hard water, and surface active and effective detergent properties, such as the reaction products of higher alcohols and higher fatty acids with considerable amounts of alkylene oxides. Numerous examples of such detergents are mentioned in Lind's U. S. Patent No. 2,396,278.

The nature of the soap or synthetic detergent employed in making the compositions of the present invention is not critical insofar as concerns compatibility with the alkali-stable class of coumarins defined herein. These coumarins are compatible with any and all known soaps and synthetic organic detergents—whether anionic, non-ionic, or cationic—and may advantageously be used to whiten all such detergents. The outstanding benefits of the invention are however realized, as will appear, in detergent compositions of an alkaline nature, and in the formulation of such compositions one tends to avoid using detergents which lack alkali stability, such as some of the cationic detergents which are hydrochlorides.

Beta methyl umbelliferone and the other coumarin derivatives which have heretofore been recommended as whitening or brightening agents are unstable in alkaline media, particularly at elevated temperatures, and their use in soaps and other detergent compositions of an alkaline nature is therefore greatly restricted. Some soaps are processed at comparatively low temperatures during and after the step of incorporating minor ingredients such as perfumes, preservatives, coloring matter, and fluorescent whitening or brightening agents, and in these soaps the unstable fluorescent agents may perhaps be used with at least temporary effectiveness. Even in such cases, however, discoloration difficulties are prone to occur when the soap is exposed to sunlight or when packing scrap is remelted, because the decomposition products produced by the attack of alkali on unstable fluorescent materials such as beta methyl umbelliferone are frequently highly colored compounds.

Objects of the invention are to provide soaps, soap compositions, and alkaline soap and/or synthetic detergent compositions generally, which have been whitened or brightened by the incorporation of alkali-stable blue fluorescing compounds, and which will not lose appreciable fluorescence with age, or discolor in sunlight or upon remelting.

Another object of the invention is to provide heat processed detergents of alkaline reaction which are whitened or brightened by the incor-

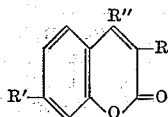
poration of fluorescent coumarin derivatives which are stable to alkalis under severe processing conditions.

Another object is to provide soap bars, granules, and flakes, and similar solid form products made from synthetic detergents in conjunction with alkaline materials, having improved whiteness by virtue of the incorporation of heat-stable and alkali-stable normally colorless compounds which in sunlight fluoresce in the blue end of the spectrum.

Another object is to provide detergent compositions (including soaps processed at low temperatures) of more permanent whiteness, due to the inclusion of blue fluorescing substances which do not gradually lose this fluorescence in mildly alkaline media at ordinary temperatures, and particularly upon prolonged exposure to sunlight.

The general terms blue-fluorescing, or fluorescing in the blue end of the spectrum, unless specifically applied to some one chemical compound, are used herein to designate fluorescence in the violet-blue-green region of the visible spectrum.

The essential whitening (or brightening) agent of the whitened (or brightened) detergent compositions of our invention is a coumarin derivative having the general formula

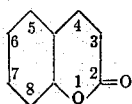


in which R is an alkyl or aralkyl group having a saturated carbon atom adjacent to the coumarin ring and containing no more than 15 carbon atoms, R' is hydroxy, amino, mono- or dialkyl-amino, mono- or dialkylolamino, or heterocyclic amino, and R'' is either alkyl or hydrogen, the number of carbon atoms in each of said R' and R'' groups in no case exceeding 6.

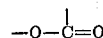
Representative of this class of alkali-stable blue fluorescing compounds, all members of which are suitable for use in the invention, are:

3-isopropyl-7-hydroxycoumarin
3-isopropyl-4-methyl-7-hydroxycoumarin
3-hexyl-7-aminocoumarin
3-butyl-7-diethylaminocoumarin
3-benzyl-7-piperidinocoumarin
3-benzyl-4-ethyl-7-methylaminocoumarin
3-benzyl-4-methyl-7-hydroxycoumarin
3-benzyl-4-methyl-7-diethylaminocoumarin
3-benzyl-7-diethylaminocoumarin
3-cyclohexyl-4-methyl-7-hydroxycoumarin
3-methyl-7-hydroxycoumarin
3-ethyl-7-hydroxycoumarin
3-ethyl-4-methyl-7-dimethylaminocoumarin
3-diphenylmethyl-4-methyl-7-hydroxycoumarin
3-isopropyl-4-propyl-7-diethanolaminocoumarin

Compounds of this general class differ from the more common coumarin-type whitening agents chiefly in the inclusion of the R group. For maximum alkali-stability we prefer to employ a comparatively large and/or branched R group, such as benzyl and isopropyl. Although we do not wish to be bound by any theory, it is our opinion that compounds which lack the R group in the 3 position, when using the following system of numbering



lack alkali stability because of the susceptibility of the unprotected lactone grouping



to attack by alkali, whereas the presence of the R group in a protective position appears effectively to hinder such attack. At any rate, otherwise similar compounds differ remarkably in the permanence of their characteristic fluorescent behavior, depending on whether or not they contain this R group. This is illustrated by the following typical data, measured under carefully standardized test conditions.

Compound	Initial fluorescence intensity in absence of alkali	No. of hrs. in alcoholic KOH at 56° C.	Fluorescence intensity in arbitrary units
4-methyl-7-hydroxy-coumarin	288	0 1 1/2 5	54 35 25
4-methyl-7-diethyl-aminocoumarin	705	0 1 5	100 39 38
7-hydroxycoumarin	606	0 1 5	72 24 26
3-benzyl-4-methyl-7-hydroxy-coumarin, *	353	0 5 100	375 285 135
3-isopropyl-4-methyl-7-hydroxycoumarin, *	196	0 5 100	310 235 90

*The starred compounds are representative of those used in the invention.

It will be appreciated that the above tests, which indicate the stability of the fluorescence in a saturated alcoholic solution of caustic potash, are much more drastic than any conditions met in the manufacture of commercial detergent products. Comparisons under more practical conditions are given in connection with following specific examples of the invention.

Example 1

(a) To a quantity of molten kettle soap at a temperature of about 200° F.—the soap being sodium soap of the fatty acids of coconut oil and tallow of good quality—was added with stirring 0.002% by weight of 4-methyl-7-hydroxycoumarin (beta methyl umbelliferone, an alkali-unstable blue fluorescer) dissolved in about 10 times its weight of essential oils perfume. A small sample of the soap was promptly removed and quickly solidified by cooling. The main mass of soap was heated to 435° F. under sufficient pressure to prevent steam formation, and was then quickly released into a flash drying chamber. A sample of the flash dried soap, which had now lost between one third and one half of its original moisture content, was removed and quickly solidified.

(b) Another lot of the same soap was similarly processed, except that 3-benzyl-4-methyl-7-hydroxycoumarin was substituted in place of the corresponding unstable derivative used in (a), and the amount of fluorescer used this time was 0.003%.

(c) Another lot of the same soap was similarly processed, except that this time 0.01% of 3-isopropyl-4-methyl-7-hydroxycoumarin was used as the fluorescer.

(d) Another lot of the same soap was similarly processed, except that to it no fluorescing compound was added.

Examination and testing of the samples from these four lots of soap showed the following:

form, containing about 0.01% of the coumarin derivative, has an enhanced whiteness in day-

Fluorescer used.....	(a) 4-CH ₃ -7-OH coumarin	(b) 3-benzyl-4-CH ₃ -7-OH coumarin	(c) 3-isopropyl-4-CH ₃ -7-OH coumarin	(d) None
Appearance of fresh samples:				
(1) Before flash drying— In daylight.....	Whiter than (d).....	Whiter than (d).....	Much whiter than (d).....	Yellowish cast.
In ultra-violet light.....	Fairly strong bluish fluorescence.	Strong greenish-white fluorescence.	Strong bluish-white fluorescence.	No fluorescence.
(2) After flash drying— In daylight.....	Pink discoloration.....	Whiter than (d).....	Whiter than (d).....	Yellowish cast.
In ultra-violet light.....	Faint fluorescence.	Strong bluish-white fluorescence.	Strong bluish-white fluorescence.	No fluorescence.
Appearance of aged samples:				
(1) Before flash drying.....	Much of whiteness and fluorescence gone.	No discoloration. Still whiter than (d). Very little loss of fluorescence.	No discoloration. Slightly whiter than (d). Some loss of fluorescence.	No appreciable change.
(2) After flash drying.....	Discolored and nearly all fluorescence gone.			

The aging referred to in the above table comprised holding the sample for 7 hours at 80° F. under strong ultraviolet light, this being equivalent to about 2 days' exposure to summer sunlight.

Example 2

0.10% by weight of 3-isopropyl-4-methyl-7-hydroxycoumarin was incorporated, as a solution in a perfume made of a mixture of essential oils, in a molten well mixed mass consisting of 70 parts of laundry kettle soap and 30 parts of aqueous sodium silicate solution. This mixture was heated (under pressure) to about 180–225° F. and forced through atomizing nozzles into the upper portion of a spray drying tower where it encountered a stream of gases having a temperature of about 300° F. The resulting laundry soap granules were very noticeably whiter than a corresponding product containing no added fluorescing material, and this improvement in whiteness was retained undiminished during a prolonged period of storage under summer warehouse temperature conditions.

Example 3

0.01% by weight of 3-benzyl-4-methyl-7-hydroxycoumarin was incorporated, as a solution in alcohol, in a molten white kettle soap to which was also added minor proportions of perfume and preservative. The mass was introduced into the hopper of a water cooled soap roll, upon the surface of which a film of the soap was converted to plastic condition. This film was cut into ribbons, which were peeled off the cooling roll and fed into a soap flake drying chamber. The resulting soap flakes or chips appeared decidedly whiter in daylight than similar soap flakes containing no blue fluorescing material. This improvement in whiteness persisted indefinitely.

Example 4

As another example, to a 10,000 pound batch of a liquid slurry containing 4160 pounds of water, 1160 pounds of a mixture of sodium salts of sulfated higher alcohols derived from coconut oil and sodium salts of sulfonated alkyl benzene (the alkyl groups being predominantly tetrapropylene), 990 pounds of sodium sulfate, 3240 pounds of sodium tripolyphosphate, and 450 pounds of miscellaneous minor ingredients, is added while agitating the batch 0.007% of 3-benzyl-4-methyl-7-hydroxycoumarin. The slurry, heated to about 160° F., is pumped to atomizing nozzles at the top of a spray drying tower through which heated air was circulated. The resulting detergent composition in granular

light which persisted indefinitely under normal conditions of storage, shipment, and use.

In the above examples one may satisfactorily replace the 3-benzyl-, or the 3-isopropyl-4-methyl-7-hydroxycoumarin with any other coumarin derivative having the aforementioned general structural formula. Frequently one may wish to adjust, within the broad limits mentioned in the following paragraph, the percentage used so as to make allowance for differences in the fluorescence intensities of the different compounds. Some of these are weaker and some are stronger than the intensities of the particular compounds used in the foregoing examples. A diethylamino group in the 7 position, for example, has in some cases been found to impart greatly increased intensity of fluorescence in the blue region, as compared to an hydroxyl group in this position. On the other hand, the substitution of —NH₂ in place of —OH in the 7 position has been found to decrease slightly the fluorescent intensity of some compounds. In addition to variations in intensity, slight differences in the hue of the fluorescent radiation are caused by changes in the structure of the molecule.

In general, the amount of alkali-stable blue fluorescing coumarin derivative which may most advantageously be incorporated in detergent compositions lies between about 0.0005% and 0.25% by weight, depending on such factors as the natural color and physical form of the untreated detergent composition, the nature of its processing, the fluorescent intensity and hue of the brightening agent used, and the amount of whitening or brightening desired. Under conditions most frequently encountered the amount of brightening agent used will be between about 0.001% and 0.10% of the weight of the detergent.

Methods of synthesizing the alkali-stable coumarin derivatives used in the invention may follow known practice. 3-benzyl-4-methyl-7-hydroxycoumarin, for example, may be prepared by a Von Pechmann condensation (Berichte 16, 2122 (1883)) of resorcinol and alpha-benzylacetoacetic ester. We have prepared this coumarin derivative by gradually adding a mole of alpha-benzylacetoacetic ester to a solution of one mole of resorcinol in sulfuric acid, cooled in an ice bath. After standing overnight, the reaction mixture was drowned in ice and water. The filtered precipitate was recrystallized twice from alcohol, dissolved in sodium hydroxide and reprecipitated with powdered Dry Ice, and recrystallized twice from alcohol with charcoaling. The product melted at 226.3°–227.0° C.

ANALYSIS

	Found	Theoretical for $C_{17}H_{14}O_3$
	Percent	Percent
carbon.....	76.57	76.67
hydrogen.....	5.39	5.30

The ultraviolet absorption maximum for this compound was found to occur at 326 millimicrons.

Similarly, 3-isopropyl-4-methyl-7-hydroxycoumarin may be prepared by condensing resorcinol and alpha-isopropylacetoacetic ester, giving a product melting at 223.8°–225.0° C.

ANALYSIS

	Found	Theoretical for $C_{17}H_{14}O_3$
	Percent	Percent
carbon.....	71.38	71.54
hydrogen.....	6.47	6.47

The ultraviolet absorption maximum for this compound was found to occur at 323 millimicrons.

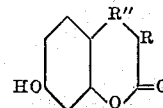
When a 7-hydroxycoumarin having no substituent in the 4 position is desired resorcinol may be condensed with an appropriate malic acid derivative or with the appropriate derivative of ethyl formylacetate. For example, the 3-methyl-7-hydroxycoumarin may be formed by condensation of resorcinol and ethyl alpha-formylpropionate (Michael, Ber. 38, 2099) and 3-ethyl-7-hydroxycoumarin by condensation of resorcinol and ethylmalic acid (Fichter and Goldhaber, Ber. 37, 2382).

When an amino group is desired in the 7 position of a 4-methyl coumarin derivative, the appropriate meta amino phenol is reacted with the appropriate acetoacetic ester. For example, 3-ethyl-4-methyl-7-dimethylaminocoumarin may be prepared by condensation of m-dimethylaminophenol and alpha-ethyl acetoacetic ester (Von Pechmann and Schaal, Ber. 32, 3695).

Having thus described our invention, what we

claim and desire to secure by Letters Patent is:

1. A solid form detergent composition of alkaline nature having an enhanced whiteness in sunlight, comprising essentially an alkaline detergent selected from the group consisting of (a) water soluble alkali metal salts of higher fatty acids, and (b) non-soap anionic synthetic organic detergents; and, in a proportion of from about 0.0005% by weight to about 0.25% by weight, coumarin derivative having the structural formula



in which R is a radical of the group consisting of alkyl and aralkyl, said radical having a saturated carbon atom adjacent to the coumarin ring and containing no more than 15 carbon atoms, and R' is a member of the group consisting of hydrogen and alkyl of not more than 6 carbon atoms.

2. The product of claim 1 in which the coumarin derivative is 3-benzyl-4-methyl-7-hydroxycoumarin.

3. The product of claim 1 in which the coumarin derivative is 3-isopropyl-4-methyl-7-hydroxycoumarin.

4. The product of claim 1 in which the detergent ingredient is sodium soap.

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