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Trimmer et al.

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[54] **LAUNDRY PRODUCT CONTAINING MIXED DYE BLUING AGENTS**

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[52] **U.S. Cl.** ..... **252/526**, 8/41 R, 8/26, 8/77, 252/527, 252/539, 252/543, 252/545, 252/546, 252/558

[51] **Int. Cl.** **C11d 3/066**

[58] **Field of Search** ..... 8/77, 25, 41 R, DIG. 14

[56] **References Cited**

UNITED STATES PATENTS

2,930,760	3/1960	Gebhardt	252/110
2,893,818	7/1959	Millsaps	8/77
539,699	5/1895	Moeller	260/182
579,773	3/1897	Rudolph	260/183
1,889,732	11/1932	Strusser et al.	260/183
2,656,099	10/1953	Selling	235/61
2,506,020	5/1950	Grossmann et al.	8/25
2,342,191	2/1944	Grossmann	8/25
3,467,645	9/1969	Keller et al.	260/174
3,445,451	5/1969	Grimmel et al.	260/148
2,141,589	12/1938	Bishop	8/77

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[57] **ABSTRACT**

A laundry product, such as a detergent composition, containing a mixture of dyes which results in laundry washed with the detergent being "blued" to a desired extent and with the desired shade of blue. The dyes employed are used in very small quantities, have little effect on the color of the laundry product, if it is in solid particulate form, are stable in alkaline media, such as crutcher mixes, and are readily bleachable by hypochlorite bleaches, so that objectionable overbluing effects need not be obtained on repeated washings. Preferred dyes employed are those of Index Numbers 24410 (Geigy, C.I. Direct Blue 1) and 29120 (Geigy, C.I. Direct Violet 66).

8 Claims, 2 Drawing Figures

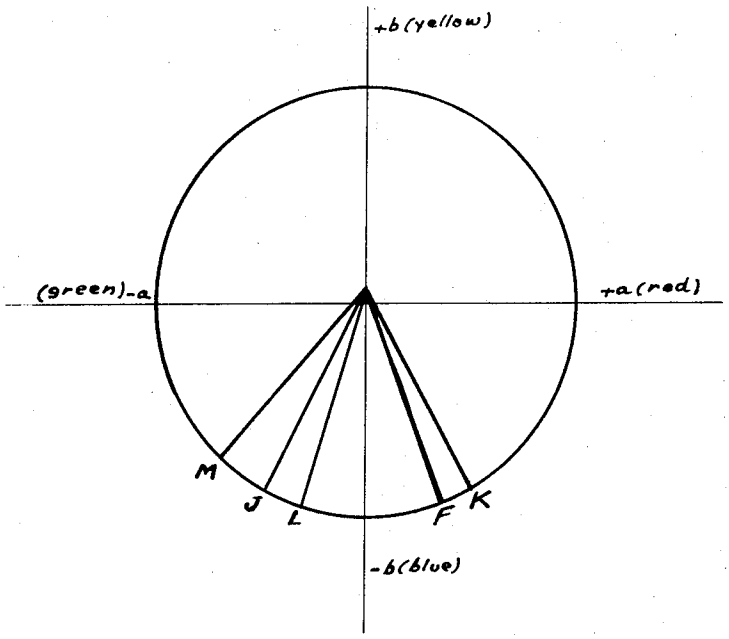
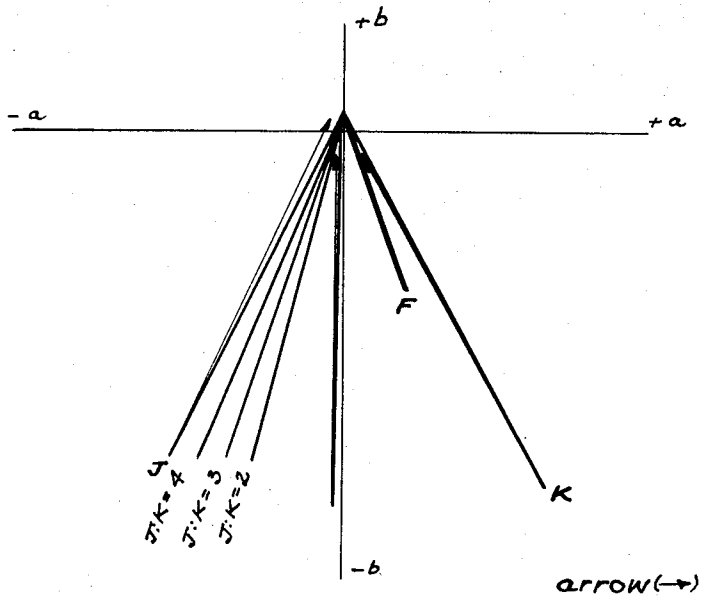


Fig. 1



arrow (→) indicates effect of bleach

Fig. 2

LAUNDRY PRODUCT CONTAINING MIXED DYE BLUING AGENTS

This invention relates to a method of "bluing" fabrics or improving the apparent whitenesses thereof by treating them with aqueous solutions of mixtures of bluing dyes. More particularly, the invention is of applications to the fabrics, especially cotton fabrics, of very dilute solutions of the mixed dyes, which dyes are so chosen as to produce the desired bluing or whitening effects in combination, with such results being attributable, at least in part, to the dyes' similar substantivities and stabilities in the solutions from which they are applied and on the dried treated fabrics. The invention also relates to the compositions employed and methods for the manufacture thereof.

The average person appears to favor white articles, such as washed fabrics, which have a slight blue cast to them. In other words, true white, i.e., achromatic white fabrics, in the opinions of most housewives, are not as white or pleasing in appearance as similar fabrics which have been blued. Therefore, it has been known to treat materials with bluing agents to improve their appearances. Dyes and pigments have been added to detergent compositions and other products for the treatments of fabrics so as to impart a blue appearance to the materials treated. Some of these dyes have been found to have undesirable characteristics, being changed in hue and converted to different and undesirable colors by chemical actions, such as bleachings. In some washing products, especially those containing blue pigments, the colors tend to be deposited on the fabrics to a similar extent with each treatment and repeated treatments can cause objectionable buildup to the extent that the bluing is no longer favored but is considered to add objectionable color, destroying the whiteness of the materials treated.

Fluorescent dyes, sometimes called optical brighteners or optical bleaches, convert ultraviolet light to visible light. They have been utilized in compositions for brightening or whitening materials, e.g., detergents. A large proportion of the most acceptable fluorescent brighteners impart to the materials treated a similar reddish blue or violet cast, which is not as much preferred as a neutral blue or a less reddish tint on washed materials.

Although the products for cleaning and whitening clothing, textiles and other materials, such as those made of cotton, wool, linen, synthetics (including nylons, acetates, polyesters, rayons and synthetic blends) and blends of natural and synthetic materials, e.g., cotton-polyester blends, have been improved greatly in recent years, before the present invention there still existed the problems of producing the most desirable "white" bluings of washed materials, preventing buildups of the bluings to the point where they could become objectionable, allowing removal of the bluings entirely, if so desired, having formulation flexibilities so that products of colors different from those of the bluing agents could be utilized and being able to produce the products by desired manufacturing methods without losses of dyeing effects, due to chemical or other degradations. Now, by following the present method, the fabrics treated may be whitened to the desired degree with the very minor proportions of dyes being employed, the products may contain colored dots, may be made of other colors or may be white in appearance,

and competitive, commercial production methods may be employed. All this is accomplished at a minimum of expense.

In accordance with the present invention, a method for increasing the apparent whiteness of a fabric comprises applying to the fabric an effective amount, up to about 3 parts per million parts of said fabric, by weight, of a mixture of compatible blue dyestuffs, of different shades and substantially the same substantivity to the fabric, in an aqueous solution at a concentration of from about 0.01 to 0.2 parts per million and in a proportion within the range of 1:5 to 5:1, said proportion being such as to produce a fabric which, when dried after treatment, is of an improved whiteness and an improved slightly blue tint, said tint being bluer than the color of fabrics washed without the presence of said dye mixture. In a preferred aspect of the invention, the dyes are incorporated in a detergent composition with a mixture of fluorescent brighteners, synthetic anionic-nonionic detergent mixture and builders, and the dyeing treatment is effected during a washing operation.

The important features of the present invention are the selection of a plurality of dyes, usually two dyes but more may be used, rarely more than five, of similar substantivities to the materials being washed and of similar susceptibilities to removal from such materials. The balanced dyes will give a desired white or barely perceptible neutral blue shade to the wash or materials treated, will not be significantly changed in hue by the usual chemical treatments, e.g., hypochlorite or per-compound bleaching, and will maintain the desired shade of blue on the dried fabric between treatments. By use of a plurality of dyes to obtain a desired shade, proportions may be adjusted for different consumer preferences. Changing of dye proportions will also be useful to produce the desired color when other materials of the composition, e.g., fluorescent brighteners, colored detergent or builder dots or fluorescent pigments are also contributing color to the treated fabric.

Another important feature of the present invention is in the removability of the dyes by simple hypochlorite bleaching. This prevents excessive buildup of bluing. If it should be decided that such buildup is wanted to some extent and if bleaching is important to remove stains or for other purposes, per-compound, e.g., perborate bleachings may be effected without destroying the dye colors. The present dyes may be incorporated in alkaline solutions or slurries, which are utilized in most washing, soaking and crutching operations. Thus, in summary, the present invention is one wherein, for very little expense, desired controllable bluing may be obtained, the bluing may be removed, and the product is so lightly colored by the bluing agents that other colors or whitening agents which may be present will have significant color effects on the product appearance. Dye hues will not be altered by bleaching chemicals or other treatments of the fabrics.

A significant concept of the present invention is illustrated by the drawing, taken in conjunction with the accompanying description. In the drawing,

FIG. 1 is a graphical representation of the hues of various dyes applied to cotton from aqueous solutions such as detergent solutions; and

FIG. 2 is a graphical representation, similar to that of FIG. 1, in which hues of greenish blue and reddish blue dyes on fabrics are shown separately, the hue of a mixture thereof in the presence of fluorescent brighteners

is illustrated and the bleaching out of the dyes by a hypochlorite solution is demonstrated.

It will be noted that the $+a$ axis of the figures indicates the degree of redness and the $-a$ axis shows the degree of greenness. Similarly, the $+b$ axis indicates yellow and the $-b$ axis is for blue. By choosing a combination of dyes identified as J and K or L and M, a color can be produced on treated fabric which is intermediate the colors of the dyes chosen and, in those cases such as are illustrated in FIG. 2, where the reddish tint of a fluorescent brightener is present, the proper choice of dyes ratio can make the treated fabric look neutral blue. The arrows on the lines of FIG. 2 represent the degree of the bluing obtained in a single typical laundry washing and hypochlorite bleaching effected after washing with the dye in the washing product. In the case of perborate or other per-compound or peroxide bleaching, significantly less dye removal is obtained, usually from one-tenth to one-third of the bleaching effect with hypochlorite being noted at normal washing temperatures, e.g., 120°–140°F. The dyes designated by J, K, L and M are identified further in the following description.

As is shown in FIG. 1, dyes J, L and M are bluish green and the ordinary fluorescent brighteners and dye K are reddish blue. It will be seen that by choice of a proper combination of dyes, e.g., a 1:3 ratio of the reddish blue to greenish blue dyes (K and J), the color of a laundering composition containing hue F fluorescent brighteners may be brought back to a neutral blue. A similar result may be obtained by use of the right mixture of dyes L and M. It must be stressed that fabrics washed will reflect much white light and the brightener will still emit white light but the violet tint thereof will be changed to neutral blue. The total effect will be a bright white fabric, slightly tinted neutral blue, rather than yellow, as may be the case in ordinary washes, without dyes or brighteners, or violet, as when brighteners are present without the bluing dyes. By choice of the best of a plurality of ratios of different similarly substantive bluing dyes, best bluing effects may be obtained with any mixture of the variety of available brighteners, all of the commercial types of which appear to have a violet tint.

As is illustrated in FIG. 2, dyes J and K, when on cotton subjected to a conventional hypochlorite bleaching in accordance with manufacturer's instructions for aqueous sodium hypochlorite bleaches, were completely bleached and the cottons were returned to a nearly achromatic white. Such results are also obtained when bleaching is effected during a washing operation. Furthermore other textiles, such as the synthetic polymerics or blends which had been "blued" with the dyes, had essentially all of the color removed. The effects of the fluorescent brightener are also sometimes lost after bleaching although some brighteners are bleach-resistant. Thus, the resultant neutral blue color illustrated can be completely removed. When sodium perborate bleaching is effected, at a temperature of about 120°F., a realistic machine washing water temperature in the United States, only about one-third of the dye is removed. Thus, a housewife may choose which bleach she wants to employ and by proper choice regulate whether or not the bluing of the present dye mixture should be maintained on the fabric or should be removed. Also in FIG. 2 are shown resultant colors obtainable by utilizing various ratios of the dyes J and K. It is noted that none of the perborate, other per-compound or hypochlorite bleaches changes the hue of the present dye mixtures.

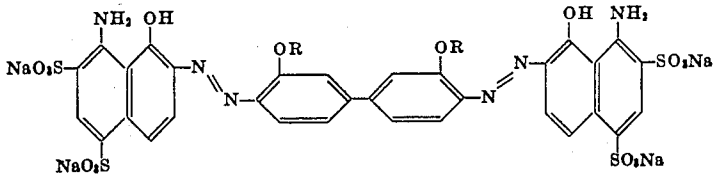
The mixture employed will preferably be of a concentration to give the proper "bluing" of the most substantive material in the laundry. Thus, in most cases cotton is the most attractive fabric to dyes and therefore, the concentrations of the dyes will be chosen so as not to overblue cotton. True, the degree of bluing of less sorptive materials may be lower but they will usually also take up less fluorescent dye and therefore, will generally have the desired hue.

Although primarily useful in detergent compositions, especially particulate detergents, such as spray dried beads or granular products, the invention may be utilized with other laundry products, in solid, bar, cake, particulate solid, paste, gel, solution, dispersion, and emulsion or other forms. Thus, the compositions may be employed in heavy duty synthetic organic detergents, light duty synthetic organic detergents, compositions which are intended primarily for their bluing action, fabric softeners, germicides, fungicides, pre-soak laundry products, starches or other fabric conditioning compositions and even bleaches. The rest of the following description will be primarily with respect to the most preferred embodiments of the invention, the spray dried heavy duty detergents, but the teachings thereof will be seen to be applicable to others of the products mentioned.

The mixture of compatible blue dyestuffs includes dyes which contain in their structures a plurality of nuclear radicals selected from the group consisting of substituted and unsubstituted cyclohexyl, phenyl, naphthyl, anthracenyl and anthraquinonyl, at least one of which is substituted with a sulfonic acid or metal sulfonate group, preferably an alkali metal sulfonate, e.g., sodium sulfonate, and at least one of which is linked to another nuclear radical of the desired class by an azo or amino group with remaining linking groups between such radicals being selected from amino, azo, $-NHSO_2-$ and a direct carbon to carbon bond. In preferred embodiments of the invention there are present two substituted naphthyl groups and two substituted phenyl groups, the phenyl substituents being selected from the group consisting of lower alkoxy (of up to three carbon atoms), hydroxy, sulfonic acid, sulfonate, and sulfonamide, and the naphthyl substituents being selected from the group consisting of amino, sulfonic acid, sulfonate, and hydroxy, with at least two azo groups being present in the molecule, linking the substituted phenyl and substituted naphthyl groups. Although in some of these compounds the phenyl groups may be linked together directly, as in diphenyl, the naphthyls are preferably linked by an amino group in those cases where diphenyl linkages are not present. Similar linking may be effected between cyclohexyl radicals, present in place of the substituted phenyl groups, and in such cases linkages, which may be to naphthyl, anthraquinonyl or anthracene groups may be through amino or sulfonamide radicals.

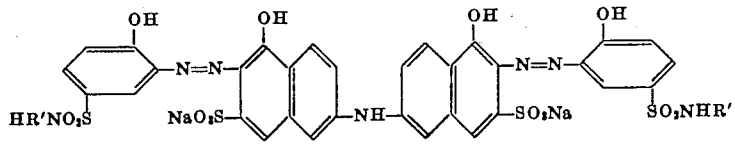
Preferred dyes which meet the requirements of the invention are of the structures:

Dye J (general formula)



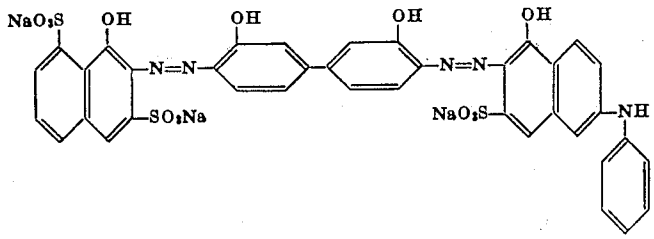
wherein R is hydrogen or lower alkyl, of one to three carbon atoms,

Dye K (general formula)



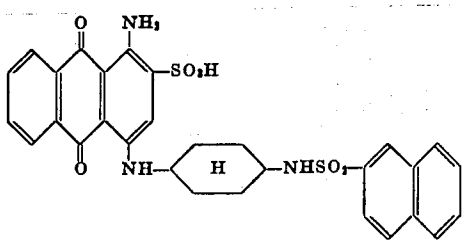
which is utilized as the corresponding bis copper complex, wherein R' is hydrogen or lower alkyl, of one to three carbon atoms,

Dye L



which is also manufactured as the corresponding bis Cu complex, and

Dye M



which may be made by the method of U. S. Pat. No. 2,740,796. Of course, the various dyes may be used in appropriate acidic or salt form and equivalent modifications of the described structures are also useful.

Preferred dyes are those wherein the lower alkyl groups R and R' are methyls. The dyes identified as J and K, marketed by Geigy Corp. under the tradenames Direct Brilliant Sky Blue 6 B Extra Conc. and Solophenyl Violet 4 BL, are especially useful. Reference numbers for these dyes are 24410 (C. I. Direct Blue 1) and 29120 (C. I. Direct Violet 66). Dyes L and M are marketed by the Verona Dyestuffs Division of Verona Corp. The former is identified as Sirius Super Blue BRL, Reference No. 23155 (Direct Blue 98). Instead of dye K, a similar dye, Sirius Supra Violet BL may be employed.

Of course, the above dyes are only exemplary of dyes preferably employed and those of skill in the art, with the guidance of the present specification, will be able to select other such dyes of balanced properties to effect the purposes of this invention.

In detergent compositions, in which the mentioned dye mixtures are preferably employed, the active detersive ingredient is preferably an anionic detergent and the more preferred detergent composition of this type also include nonionic detergent. Mixtures of such materials and amphoterics may also be used. The anionic detergents will normally contain from eight to 26, preferably 10 to 20 carbon atoms in a higher organic hydrophobic group, and will have present at least one water-solubilizing radical selected from the group consisting of sulfonates, sulfates, carboxylates, phosphates and phosphonates, to produce a water soluble detergent. Examples of suitable anionic detergents are water soluble sulfated and sulfonated synthetic detergents containing an alkyl radical of eight to 20, preferably 12 to 18 carbon atoms. Such radical may be a portion of a higher acyl group. Preferred examples of sulfonated anionic detergents are the higher alkyl aromatic sulfonates, such as the linear higher alkyl benzene sulfonates containing from 10 to 18 atoms in the higher alkyl group. Branched chain materials may also be used, but are not preferred. The sodium, potassium, ammonium and lower alkanolamine salts of such sulfonic acids are preferred. In some cases, higher alkyl toluene sulfonates and higher alkyl naphthalene sulfonates may be beneficially employed. Of the linear alkyl benzene sulfonates, those of 12 to 15 carbon atoms in the chain and wherein the salt forming cation is sodium are much preferred. These usually will be terminally or 2-substituted on the benzene ring. However, other points of joinder to the benzene may be employed and the main factor in producing a successful detergent of this type is to have the chain linear so as to promote biodegradability of the product.

Included among other anionic detergents which may be employed are the olefin sulfonates, e.g., long chain alkene sulfonates, long chain hydroxyalkane sulfonates and mixtures thereof. These are usually of eight to 25

carbon atoms, preferably of 12 to 20 carbon atoms. Also useful are the paraffin-derived sulfonates containing about 10 to 20, preferably 15 to 20 carbon atoms. Examples are the primary paraffin sulfonates made by reaction of long chain alpha olefins with bisulfites and those compounds having the sulfonate group distributed along the paraffin chain. Sodium and potassium sulfates of higher alcohols containing eight to 18 carbon atoms, such as sodium lauryl sulfate and sodium tallow alcohol sulfate may be employed, as may be the sodium and potassium salts of alpha-sulfofatty acid esters of 10 to 20 carbon atoms in the acyl group, e.g., methyl alpha-sulfomyristate and methyl alpha-sulfotallowate. The sodium and ammonium sulfates of mono- and diglycerides of higher fatty acids, e.g., coconut oil fatty acids monoglyceride monosulfate, stearic diglyceride monosulfate, are also useful, as are the sulfated condensation products of polyethoxyethanols with fatty alcohols and the sulfonates of higher alkyl glycerol ethers. The alkyl phenyl polyethoxy ether sulfates having about one to six oxyethylene groups per molecule are useful anionic detergents when the alkyls are of about seven to nine carbon toms. Such a range of carbon atoms is considered as "middle" alkyl. Other useful anionic detergents include the higher acyl sarcosides, isethionates and N-methyl taurides. These detergents, while normally used as their ammonium, alkanolamine, or alkali metal salts, may often be employed as soluble alkaline earth metal salts. The water soluble salts, e.g., the sodium, ammonium and alkanolamine salts, of higher fatty acids containing about eight to 20 carbon atoms, preferably 10 to 18 carbon atoms, are good anionic detergents, too. The suitable fatty acids for making such soaps can be obtained from animal and vegetable oils, fats and waxes, e.g., tallow, grease, coconut oil, tall oil and various mixtures thereof. Preferred are the sodium soaps of the fatty acids derived from the mixture of coconut oil and tallow.

The nonionic synthetic organic detergents are usually condensation products of organic aliphatic or alkyl aromatic hydrophobic compounds and hydrophilic lower alkylene oxide groups. A wide variety of hydrophobic compounds which include carboxy, hydroxy, amido or amino groups having a free hydrogen on the nitrogen can be condensed, with a lower alkylene oxide or equivalent, such as ethylene oxide, polyethylene oxide, or polyethylene glycol to form the nonionic detergents. Useful hydrophobes are higher aliphatic alcohols, middle alkyl phenols, higher fatty acids, carboxamides, mercaptans and sulfonamides. The ethylene oxide condensates of such materials usually include from 5 to 50 moles of ethylene oxide but as many as 200 moles may often be present. The hydrophobic groups will generally contain at least about six carbon atoms but may contain as many as 50. A preferred range is from about eight to 30 carbon atoms in the hydrophobe. The ethylene oxide or the corresponding glycols or polyderivatives thereof are preferred but other lower alkylene oxides, such as propylene oxide, may also be of use and in some cases butylene oxide can be employed, generally in minor proportions. Other nonionic compounds included as active detersive ingredients are the polyoxyalkylene esters of higher fatty acids which will generally contain from 12 to 30 moles of ethylene oxide per mole of fatty acid of 10 to 22 carbon atoms. The alkylene oxide condensates of higher fatty acid amides are useful and these will usually have present from 10 to 50 moles of ethylene oxide per mole of eight to 22 carbon atom fatty acid group. Corresponding carboxamides and sulfonamides are also useful. Oxyalkylated higher aliphatic alcohols are especially preferred nonionic compounds, utilizable in conjunction with the linear higher alkyl benzene sulfonate anionic detergents. The fatty alcohols will usually have from 10 to 18 carbon atoms and the polyoxyethylene group will contain from 6 to 30 moles of ethylene oxide, preferably from about 6 to 12 moles thereof when the alcohol is of 12 to 16 carbon atoms. Such nonionics are sold as Neodols by Shell Chemical Co.

Hydrophobic groups of the nonionics can be made by condensing polyoxypropylene or polyoxybutylene radicals, in which case the subsequent condensation with ethylene oxide or polyoxyethylene groups results in the production of a nonionic detergent such as those sold under the names Ucon and Pluronic. In the Pluronics the block copolymers made are of ethylene oxide, propylene oxide and some propylene glycol and have a molecular weight in the range of about 1,000 to 15,000. The polyethylene oxide content thereof will usually be from 20 to 80 percent by weight and the preferred hydrophobic moiety weight is from about 1,000 to 4,000. Nonionics may be derived by the condensation of ethylene oxide with the reaction product of propylene oxide and ethylene diamine, in a manner similar to that employed for the preparation of the Pluronics. Various other nonionic detergents which may be used include the ethylene oxide aducts of monoesters of hexahydric alcohols and inner ethers thereof, with the higher fatty acids being of about 10 to 20 carbon atoms, e.g., sodium monolaurate, mannitan monopalmitate. Additional nonionic detergents that have been found to be very useful are the amine oxides of the general formula $R^1R^2R^3N \rightarrow O$, wherein R^1 is a higher alkyl of 10 to 20 carbon atoms and R^2 and R^3 are lower alkyls. Similar compounds wherein the nitrogen is replaced by phosphorus are also useable.

Although usually not employed in detergent compositions, amphoteric detergents are useful. These are generally water soluble salts of derivatives of aliphatic amines which contain at least one cationic group, e.g., quaternary ammonium, non-quaternary nitrogen or quaternary phosphonium, one or two alkyl groups of about eight to 18 carbon atoms and an anionic water solubilizing carboxyl, sulfo, sulfato, phosphato or phosphono group. The groups may be straight chained or branched and the cationic nitrogen or phosphorus may be in a heterocyclic ring. Examples of such amphoteric detergents include the alkyl beta-aminopropionates, the alkyl betaiminodipropionates, the alkyl and hydroxyalkyl taurinates and the long chain imidazole derivatives, such as those described in British Pat. No. 1,412,921 and U.S. Pat. Nos. 2,773,068, 2,781,354 and 2,781,357. Preferred detergents of this type are sodium N-lauryl beta-aminopropionate and disodium N-lauryl iminodipropionate.

Cationic surface active agents are usually avoided in the present detergent compositions but may be employed when there are no anionics present or when a laundry treating composition is used primarily for its antibacterial activity. Examples of the cationic detergents are the normal primary amines wherein the alkyl group is of 12 to 15 carbon atoms, and the corresponding diamines. Quaternary ammonium compounds of

the known type, preferably those having one or two higher alkyl groups and two or three lower alkyl groups attached to the nitrogen and wherein the solubilizing anion is a halogen are also useful, as are equivalent quaternaries of high antibacterial activity, which are well known in the art.

Detergent compositions in which the present dyes are incorporated may also have present builder salts, fillers, solvents and adjuvants. Typical of the builders that may be employed are the inorganic builder salts, such as alkali metal polyphosphate salts, e.g., pentasodium tripolyphosphate, tetrasodium pyrophosphate and the corresponding potassium compounds. Other builders, especially popular in formulations low in phosphate content, are alkali metal silicates and carbonates, as well as the corresponding borates and bicarbonates. Preferably, the silicates will have an $Na_2O:SiO_2$ ratio of about 1:2.35, although the range of 1:2 to 1:3 is normally useful and often ratios as low as 1:3.2 are acceptable. The organic builders that are employed are the citrates, diglycolates, gluconates, ethylene diamine tetraacetic acid, sodium salt and trisodium nitrilotriacetate. Of course, mixtures of builders may be used and they may be supplemented with fillers, which generally do not perform any significantly useful function with respect to increasing the detergency of the product. Among the fillers that are useful are the sulfates, chlorides, nitrates, and acetates, usually as their alkali metal salts, e.g., sodium sulfate. Solvents that may be employed will usually be primarily aqueous and any supplementing solvent material will generally be a lower alcohol, e.g., ethanol, isopropanol, or a polyol, e.g., polyethylene glycol, glycerol, if present at all. Of course, other organic solvents may be present, as in emulsions.

The various adjuvants that are used, in addition to the fluorescent dyes, include germicides, fungicides, perborate bleaches, enzymes, soil suspending agents, fabric softeners, thickeners, corrosion inhibitors, sequestrants, tarnish inhibitors, perfumes and various other materials intended to improve the functional and aesthetic properties of the detergents. Such materials are well known in the art and need not be described at length here.

Among the additives for detergent compositions are materials which may be employed alone in other laundry preparations with the present dye mixtures. For example, enzymes may be added to detergents or may be incorporated in a pre-soak product. Among such enzymes are those of the proteolytic type, including subtilisin, bromelin, papain, trypsin and pepsin. Soil suspending materials, e.g., sodium carboxymethyl cellulose, methyl cellulose and hydroxypropyl methyl cellulose may be in the detergent or presoak compositions. Useful bactericidal effects may be obtained by adding germicides to the detergent or by utilizing these in separate treatments after washing has been completed. Fabric softening compositions may be employed in a similar manner.

Exemplary of useful cationic softeners are distearyl dimethyl ammonium chloride, lauryl trimethyl ammonium bromide and stearyl dimethyl benzyl ammonium bromide. Such materials will also possess antibacterial properties. Other useful cationic softeners include the higher alkyl pyridine salts, higher alkyl imidazolines, higher alkyl amines and higher alkyl guanidine salts, such as 1-methyl-1-stearyl aminoethyl-2-stearyl imidazolinium methosulfate, 2-heptadecyl-1-methyl-1(2-stearoylamido)ethyl imidazolinium methyl sulfate, stearyl pyridinium halides, cetyl isoquinolinium bromide and higher alkyl morpholinium chloride. In such compounds the higher alkyls are of eight to 20, preferably of 12 to 18 carbon atoms. Amphoteric compounds which are useful as softeners include those marketed as Soromines, Deriphats, Miranols, especially Soromines AL and AT, which are complex fatty amido compounds. Included among the useful nonionic softeners are polyoxyethylene lauryl ether, sold as Brij 30; myristyl dimethyl amine oxide, sold as Textamine Oxide TA; nonylphenoxy polyethoxy ethanol, sold as Igepal CO–880; and polyoxyethylene sorbitan monostearate, sold as Tween 61. The anionic softeners and antistatic agents which are most useful are the water soluble higher fatty acid soaps and synthetic organic surface active agents of the sulfuric reaction type. Such materials were previously described in the specification with other surface active agents and detergents.

Lengthy descriptions of additional softeners are not given herein because all such compounds may be colored with the present mixed dyes and descriptions thereof may be found in the reference, *Detergents and Emulsifiers* 1969 Annual, by J.W. McCutcheon. Of course, the fabric softeners and bactericides may also contain various adjuvants, such as those previously described.

The concentration of dye mixture used will be such that an effective amount of the mixture, usually up to about three parts per million parts of a fabric to be whitened will be employed. The dyes used, being substantially equally substantive to the fabric to be treated, will improve the whiteness thereof, whether applied in dilute or concentrated solutions or for long or short periods of time. Normally, the dye mixture will be dissolved in an aqueous medium, usually over 99 percent water, so that the concentration thereof is from about 0.01 to 0.2 parts per million. with the proportions of the different dyes being in the range of 1:5 to 5:1. When applied in a detergent composition, the dye mixture will usually constitute from about 0.0005 to 0.01 percent of the detergent and the detergent will be from 0.05 to 1 percent of the aqueous wash water. The concentration of the dye mixture in laundry preparations from which it is applied to fabrics, preferably to laundered fabrics, may be the same as that for detergents but in some instances the concentrations may be cut to one-tenth the proportion in detergents, preferably no more than one-half such proportion, or may be doubled or quadrupled, depending on the amount of such products normally employed in the aqueous solution from which the dyes are applied to the fabric. The ultimate concentrations in the aqueous media will usually be approximately the same as for the detergents.

The temperatures of applications of the various laundry products and the times of contact may be varied over a fairly wide range period. Thus, from 10°C. to 90°C. is the broad range of application and a preferred range is from 40°C. to 60°C. Such range is considered "preferred" because it is the most common range of temperatures which most laundering operations are effected. The times of contact between the dye mixture solutions and the fabrics may also vary widely, being from one minute to as much as 1 hour, usually from 10 to 45 minutes. To obtain even dyeing it is generally pre-

ferred to have the dye mixture solution in active motion with respect to the fabrics or laundry being treated.

The optical brighteners employed, which will usually be known brighteners for use with cottons and synthetics, should be present in concentrations of 0.05 to 3 percent, preferably 0.2 to 2 percent and most preferably, about 0.5 to 1.5 percent of the detergent compositions or other laundry preparations of which they are constituents. Almost all of the fluorescent brighteners give a reddish blue tint to the fabric treated and the concentration of dye mixture used will be such as to produce a bluer white. Selected mixtures of the greenish blue synthetic dyestuff and the reddish blue synthetic dyestuff of this invention in which the concentrations of both dyes in the laundering compositions are in the described ranges have been effective to counteract the reddish blue tints of the fluorescent dyes and to "whiten" fabrics, even without fluorescent dyes present, especially at concentrations of detergent or laundering product in the wash water of from 0.1 to 0.5 percent.

In detergent compositions the content of dyestuff mixture is preferably from 0.0005 to 0.01 percent and the concentrations of green-blue dye and red-blue dye are from 0.0001 to 0.0004 percent, preferably from 0.001 to 0.003 percent and 0.0003 to 0.001 percent, respectively. The detergents comprise 5 to 85 percent, preferably 10 to 50 percent of synthetic organic detergent (including soap) or a mixture of such detergents, with 15 to 95 percent, preferably 25 to 75 percent, being builders, fillers, solvents and adjuvants. Clearly, when the detergents are liquid detergents the proportions of such can be comparatively high, often from 50 to 85 percent and when the products are particulate solids the proportions of builders and fillers may be high, generally from 30 to 95 percent of the combination of builders and fillers, preferably from 15 to 45 percent of builder and 15 to 50 percent of filler salt. The proportions of adjuvants will normally be small, often under 10 percent and sometimes even under 5 percent total. The most common solvent employed, water, may constitute from 50 to 95 percent of the liquid detergents and may often be from 1 to 20 percent of the content of the particulate solid detergents or other laundry products in such form. The nonionic detergent, which may accompany 5 to 30 percent synthetic anionic detergent, is usually from 1 to 10 percent of the product but may be as much as 50 percent of liquids. The proportion of nonionic is generally less than one-half the proportion of anionic detergent present. Although the range of greenish blue to reddish blue dye may be from 5:1 to 1:5, a preferred range is from 2:1 to 4:1 and the ratio of a mixture of the substantive synthetic dyestuff to the fluorescent dye is from 5:10,000 to 5:1,000. Similar considerations and concentrations apply when presoaks, bactericides, bleaches or softeners are made, with the active ingredients being present in the amounts and proportions given above for the detergents.

In highly preferred detergent compositions, such as those illustrated in the present examples, the anionic detergent, a sodium salt of a higher linear tridecyl benzene sulfonic acid, is from 7 to 15 percent of the product and the nonionic detergent, a higher fatty alcohol condensation product with ethylene oxide, is 1 to 4 percent. In such products the proportion of higher fatty alcohol to ethylene oxide, on a molar basis, is from about 1:8 to 1:14. Also, the builder salt present in this detergent is from 20 or 25 to 35 percent of pentasodium tripolyphosphate and 5 to 10 percent of sodium silicate of $Na_2O:SiO_2$ ratio of from 1:2 to 1:3. The mixture of dyes constitutes from 0.001 to 0.003 percent of the greenish blue dye and 0.0003 to 0.001 percent of the reddish blue dye. The best products described herein have from 25 to 50 percent of sodium sulfate filler present and are of particle sizes such that none are larger than the opening of a No. 8 U. S. Standard Sieve Series sieve and no more than 10 percent passes through a No. 100 sieve. However, particles within the 6 to 160 mesh range are also acceptable. Such products are preferably made by spray drying of an aqueous crutcher mix, in which the preferred builder is pentasodium tripolyphosphate.

The spray drying operation is effected from a crutcher mix containing 30 to 70 percent of normally solid materials, the balance usually being water or other suitable aqueous medium. Less than 0.01 percent of the mix present is compatible blue dyestuffs of different shades. Mixing may be carried out at suitable temperatures from room temperature (20°C.) to 90°C. and spray drying is effected through spray nozzles at high pressures, e.g., 300 to 1,000 lbs. per square inch, into a drying gas at a temperature of from 110 to about 400°C. Either concurrent or countercurrent spray towers may be employed. Due to the content of alkaline builder materials, the crutcher mix will normally have a pH in the range of from 9 to 11 and, despite such pH and the high temperatures of drying, the present dyes are not altered in color during processing.

In all cases wherein laundry is treated by application thereto of an aqueous or solvent solution or suspension of treatment materials, the presence of the mixed dyes of this invention will add a bluing effect to improve the whiteness of the treated fabrics. Of course, the laundry treating product may be in liquid, solid, paste, emulsion or other suitable form, before use.

Instead of spray drying, the dyes may be post-sprayed in solution onto detergent particles or onto a proportion of such particles. If desired, the dyes can be employed to color only a proportion of particulate solid materials, e.g., from 0.2 to 10 percent, preferably from 0.5 to 5 percent thereof. The colors may be bright if high concentrations are employed on only a small proportion of the particles or may be very light, as when the dyes are distributed evenly over all the particles. If desired other obscuring dyes may be employed, preferably "fugitive dyes" which do not have a permanent effect on the color of the fabrics treated. Such dyes include Polar Brilliant Blue RAW, Levalon Blue FFR and Acilon Sapphirol BNA; others are described in U. S. Pat. application Ser. No. 154,692 of V. Richter, for Colored Detergents, filed June 18, 1971.

The following examples illustrate the invention. Unless otherwise indicated, all parts are by weight and all temperatures are in °C. in this specification.

EXAMPLE 1

A heavy duty synthetic organic detergent intended for use in cold or warm water is made by spray drying in a countercurrent tower a crutcher mix of the following formulation:

	Parts
Water	27.1
Linear tridecylbenzene sulfonate slurry (56% solids, 87.5% active ingredient, on solid basis)	13.8
Sodium silicate (1:2.35 $Na_2O:SiO_2$ ratio)	10.9
Sodium sulfate, anhydrous	22.9
Higher fatty alcohol polyethoxylate*	1.4
Sodium carboxymethyl cellulose, 65% active	0.5
Polyvinyl alcohol	0.1
Fluorescent brighteners**	0.7
Preservative	0.02
Sodium coco-tallow kettle soap	1.0
Pentasodium tripolyphosphate	21.6
Solophenyl Violet 4BL	0.0002
Direct Brilliant Sky Blue 6B Extra Conc.	0.0007

*C 14-15 alcohol; ethylene oxide content, on a molar basis, being 11:1.

**Mixture of Tinopal RBS (20%), Stilbene Brightener for cotton, Oxazole Brightener (40%); and a major proportion of Tinopal 5 BM Conc.

The above aqueous slurry is agitated in a heated crutcher at a temperature of about 60°C., for 5 minutes after the addition of all the ingredients, after which it is pumped through spraying nozzles and is spray dried in a countercurrent spray tower, the spraying pressure being about 600 lbs. per square inch and the temperature of the drying air in the spray tower being about 350°C. Spray nozzles are sized so as to produce particles in the 6 to 160 mesh range, U. S. Standard Sieve Series. After drying, particles outside the range are screened off or otherwise separated. Moisture loss is approximately 33 percent and the final product has moisture content of about 11 percent. Subsequently, about 0.2 percent of perfume is sprayed onto the surfaces of the particles.

The product made is substantially white, with a slight blue tint. It is used to wash cotton fabrics at a detergent concentration of 0.15 percent in water of 150 parts per million hardness at 120°F. Washing is in standard washing machines for various usual wash times, about 10–30 minutes. After rinsing and drying, the washed items are compared visually by 10 panelists against a product the same as that described but without the greenish blue and reddish blue dyes. Under daylight, incandescent light and fluorescent light the panelists significantly prefer the color of the fabrics washed with the composition containing the dye mixture of this invention. The clothing and other laundry items washed with this detergent are cleaned well and are an attractive white, preferred by most people.

In a similar test, the green-blue and red-blue dye concentrations are increased approximately three-fold. When evaluated after five washes, utilizing a mixed wash load, including cottons and synthetic fabrics, e.g., polyester-cotton blends, nylons and acetate, the materials treated with detergent containing the dye mixture of this invention were preferred by more than 2:1 over a control wash. However, some panelists considered the color of the cotton items to be "almost too blue" and for such evaluators, the content of dyes may be decreased in the product. In both the above experiments, the pH's of crutcher mixes, about 10.5 and the wash water, about 9.2, do not adversely affect the stabilities of the dyes. When the laundered items are washed again with the same composition, but containing a cup of 3 percent sodium hypochlorite solution per 15 gallons wash water, the dyes of the mixture are bleached so as to result in a more achromatic white appearance of the textile. Such bleaching of a J:K = 3 dye mixture can be illustrated by considering that the J:K = 3 line, as shown in FIG. 2, returns to near the origin, only slightly on the greenish side of the "*a*" axis. When bleached with sodium perborate, at concentrations of from 2 to as much as 20 percent in the detergent composition, the dyes' color is not as strongly bleached and about two-thirds of it remains. Yet, stains on the items being washed are removed by the bleaching operation.

In preferred products the spray drying characteristics are adjusted so as to produce a product in which the particles are larger than 8 mesh and less than 10 percent pass through a 100 mesh sieve.

The same results obtain when washings effected are in soft water and in very hard water, with hardnesses being less than 50 p.p.m. and from 200 to 300 p.p.m., respectively. The shifting of the color of the product from the violet tint area to a more neutral blue is noted by the panelists and is aso verified instrumentally.

Similar results are obtained when the dyes employed are those identified as L and M but such dyes are not considered as good as J and K, because they do not permit as much color control in formulating because both dyes are greenish blue. When dyes L and M are used, preferred concentrations in the detergent are from 0.0005 to 0.001 percent of L and 0.001 to 0.002 percent of M.

The experiments detailed above are repeated, utilizing a light duty nonionic detergent containing 40 percent of nonyl phenol polyoxyethylene ether having about 15 oxyethylene groups per mole, together with 2 percent of Miranol amphoteric detergent, 10 percent of sodium sulfate and the balance of water and minor adjuvants. Such a product also blues cotton washed with it and the bluing is bleachable with sodium or calcium hypochlorite solution. Such essentially nonionic compositions can be made to contain as much as 50 percent of the nonionic and 10 percent of the amphoteric and the results described are still obtained. The nonionic detergents can be made as solutions, emulsions, pastes or creams.

In other variations of the main experiment of the formula given, proportions of synthetic organic detergent and builder-filler combination are varied to raise the content of synthetic detergent by 50 percent and decrease that of the builders 50 percent. Also, the reverse change is effected and in both instances the more neutral blue coloration obtained with the dye mixture is favored by viewers.

When the pentasodium tripolyphosphate is replaced by half as much trisodium nitrilotriacetate and the sodium sulfate content is increased accordingly, a desired neutral blue tint is still obtained. Also, such is the result when the linear tridecyl benzene sulfonate slurry is replaced by an equal quantity of sodium lauryl sulfate, sulfated polyoxyethylene lauryl alcohol or branched dodecyl benzene sulfonate, sodium salt. Similarly, such results are obtained when the content of soap is increased to 2 percent and when the proportions of fluorescent brightener are doubled or halved. When the fluorescent brightener content is changed, it is preferred to change the dye mixture content accordingly.

EXAMPLE 2

A spray dried granular laundry detergent composition is prepared of the following formula:

	Parts
Neodol 45–11	10.0
Sodium carbonate	45.0
Sodium silicate ($Na_2O:SiO_2$ = 1:2.35)	18.4
Sodium carboxymethyl cellulose	0.5
Fluorescent brighteners (violet tint)	0.8
Water	10.0
Sodium sulfate, anhydrous	15.3

Spray drying is effected using the conditions described in Example 1, with the product being in the 8 to 100 mesh particle size range. Quantities of green-blue and red-blue dyes J and K, described in the formula of Example 1, are applied from an aqueous solution to 2 percent by weight of the particles, with the resulting particles being colored a dark blue. The product is a speckled or variegated detergent powder and, upon testing, has the same properties as the product of Example 1 with respect to improving the coloration of wash materials laundered with it. In some instances, when losses of nonionics in the spray drying operation are excessive, a portion of the nonionic may be post-sprayed onto the detergent particles. In such cases, the dyes may be applied with the nonionics. In a variation of the method for making products of the above formula, the mixed dyes are added in the crutcher and after production of the detergent particles, which are light colored, a portion thereof or the entire product is colored with a fugitive dye such as Polar Brilliant Blue RAW or any of the other dyes described in U. S. Pat. application Ser. No. 154,692, referred to earlier.

When a product of the formula of Example 2 is modified by replacement of 20 parts of sodium sulfate with sodium perborate, a bleaching detergent is obtained, from which the improved neutral blue coloration of washed cotton fabrics, such as terrycloth towels and synthetic fabrics, is obtained. Upon a subsequent application of sodium hypochlorite bleach, either alone or in a detergent composition, the blue coloration is bleached out and the fabrics return to near achromatic white.

EXAMPLE 3

A laundry soap powder is made by mixing together granular materials of the following formula:

	Parts
Sodium soap of mixed coconut oil and tallow fatty acids	65.00
Sodium carbonate	11.3
Sodium silicate	10.0
Sodium chloride	2.5
Fluorescent brighteners	1.1
Perfume	0.1
Water	10.0
Greenish blue dye J	0.001
Reddish blue dye K	0.0003

The dyes are applied by spraying in dilute solution (1 percent in water) onto the surfaces of the tumbling granular mixture. The product obtained is very lightly colored and produces a more neutral blue in the laundry washed with the composition than is the case when the dyes are omitted.

EXAMPLE 4

A fabric softener composition is made of the formula:

	Parts
2-Heptadecyl-1-methyl-1[(2-stearoylamido) ethyl]imidazolinium methyl sulfate, 75% active ingredient	
Aqueous brightener solution, 23% active ingredient	1.4
Perfume	0.3
Water	88.8
J dye	0.003
K dye	0.001

In a five wash clean load test this composition is superior to a control composition in which whiteness preference under three types of light, incandescent, north daylight and fluorescent, when employed in the same final dilution as is the case for the detergent composition of Example 1. The products treated are soft and are of desired neutral blue color.

EXAMPLE 5

A pre-soak composition is made of the formula:

	Parts
Linear tridecyl benzene sulfonate, sodium salt	6.0
Sodium tripolyphosphate	25.0
Sodium carbonate	44.6
Sodium sulfate	10.0
Sodium silicate	7.0
Fluorescent brightener	0.6
Protease enzyme (Alcalase, Novo)	0.8
Moisture	6.0
J dye	0.003
K dye	0.001

After a clean load soaking test of about 1 hour, the laundry, terrycloth towels and diapers soaked in this composition, is preferred for color over controls. Also, synthetic fabric swatches give similar results. The cloths treated are more neutral blue and yet are bleachable with hypochlorite, if desired. The final concentrations of the dyes in use are similar to those described in Example 1.

When dyes J and K are replaced by L and M or other types of the invention, in the desired proportions within the ranges described in the specification, more favorable acceptable by panelists is obtained than for controls. This is also the case when the concentrations are varied within the ranges described herein.

The invention has been described with respect to illustrations and working examples thereof. Of course, it is not to be considered as limited to these inasmuch as the principles of the invention may be applied by one of skill in the art and variations may be made in the components of the compositions, treating steps and manufacturing methods which will still be within the spirit of the invention.

What is claimed is:

1. A synthetic organic detergent composition for increasing the apparent whiteness of a fabric comprising:

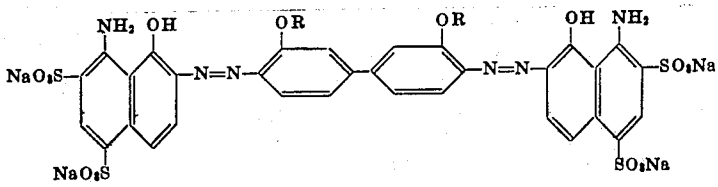
A. a mixture of water soluble compatible blue dyestuffs of such different shades so as to independently color fabrics washed therewith greenish blue and reddish blue, respectively, each of which dyes is substantially bleachable with aqueous hypochlorite bleach and contains in its structure a plurality of nuclear radicals selected from the group consisting of substituted and unsubstituted cyclohexyl, phenyl, naphthyl, anthracenyl and anthraquinonyl, at least one of which is substituted with a sulfonic acid or metal sulfonate group and at least one of which is linked to another nuclear radical of the described class by an azo or amino group, the remaining linking groups between radicals of the described class being selected from the group consisting of amino, azo, —$NHSO_2$— and direct carbon to carbon bond, said dyes being substantive to fabric and of substantially the same substantivity to cotton, said dye mixture constituting from 0.0005 to 0.01 percent of the detergent composition with the ratio of dyes within the dye mixture being within the range of 1:5 to 5:1, which proportion is such as to produce a fabric, which, after washing in aque-

ous medium with the detergent composition, is of an improved whiteness and a slightly blue tint, which tint is bluer than the color of fabrics washed with the composition, absent the dye mixture;

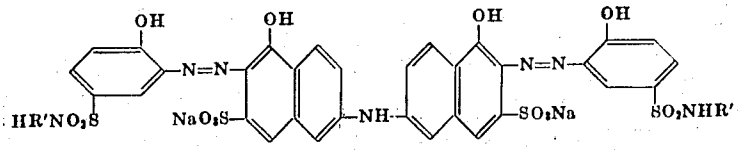
B. 5 to 85 percent of a synthetic organic detergent or mixture of such detergents selected from the group consisting of anionic, nonionic and amphoteric detergents; and

C. 15 to 95 percent of compound(s) selected from the group consisting of builder(s), filler(s), solvent(s) and adjuvant(s).

2. A detergent composition according to claim **1** wherein the greenish blue dyestuff is of the formula

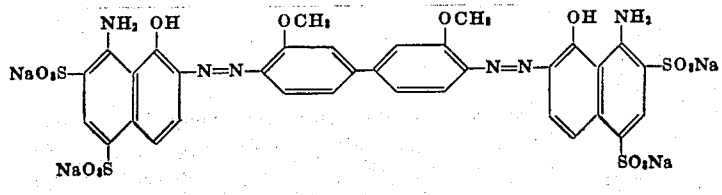


wherein the R radicals are selected from the group consisting of lower alkyls of one to three carbon atoms and hydrogen, and the reddish blue dyestuff is of the formula

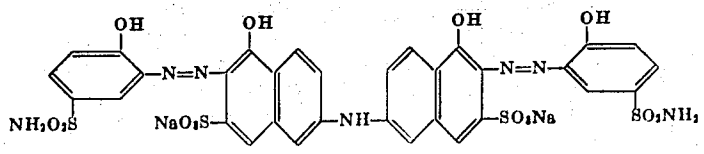


in the form of the corresponding bis copper complex and wherein the R′ radicals are selected from the group consisting of lower alkyls of one to three carbon atoms and hydrogen.

3. A detergent composition according to claim **2** wherein the greenish blue dyestuff is of the formula



and the reddish blue dyestuff is of the formula



in the form of the corresponding copper complex of the bis type.

4. A detergent composition according to claim **3** which also comprises from 0.05 to 3 percent of an optical brightener or fluorescent dye which is of apparent violet or reddish blue tint when applied to fabrics and the mixture of the described water soluble synthetic organic greenish blue and reddish blue dyes present is such that, with the fluorescent dye, the fabric subjected to contact with aqueous solutions of the detergent composition is tinted a more neutral blue than the fabric with fluorescent dye only on it.

5. A detergent composition according to claim **4** wherein the proportion of fluorescent dye is from 0.2 to 2 percent, the proportion of greenish blue synthetic dyestuff is from 0.0001 to 0.004 percent, the proportion of reddish blue synthetic organic dyestuff is from 0.0001 to 0.004 percent, the ratio of greenish blue synthetic dyestuff to reddish blue synthetic dyestuff is from 2:1 to 4:1 and the ratio of mixture of substantive synthetic organic dyestuffs to fluorescent dye is from 5:10,000 to 5:1,000.

6. A composition according to claim **5** wherein the detergent composition is a heavy duty built synthetic anionic-nonionic detergent composition in particulate form comprising from 5 to 30 percent of a synthetic anionic organic detergent or mixture thereof selected from the group consisting of linear higher alkyl benzene sulfonates, higher fatty alcohol sulfates, higher olefin sulfonates, and higher fatty acid soaps, from 1 to 10 percent of a nonionic detergent or mixture selected from the group consisting of ethylene oxide condensates with higher aliphatic alcohols, ethylene oxide condensates with middle alkyl phenols and ethylene oxide condensates with propylene oxide and propylene glycol, with the proportion of nonionic being less than one-half the proportion of anionic detergent present, and 30 to 95 percent of builder or builder mixture selected from the group consisting of pentasodium tripolyphosphate, trisodium nitrilotriacetate, sodium silicate, sodium carbonate, sodium citrate and sodium gluconate, the detergent composition being a spray dried particulate product substantially white in color or of a color different from that imparted to fabrics washed with the detergent, the particles of detergent being globular in shape and of sizes substantially within the range of 6 to 160 mesh.

7. A composition according to claim **6** wherein the

anionic detergent is a sodium salt of a higher linear tridecyl benzene sulfonic acid and comprises from 7 to 15 percent of the product, the nonionic detergent, from 1 to 4 percent of the product, is a condensation product of a higher fatty alcohol of 10 to 18 carbon atoms with ethylene oxide, with the proportion of higher fatty alcohol to ethylene oxide, on a molar basis, being from 1:8 to 1:14, the builder includes from 25 to 35 percent of pentasodium tripolyphosphate and 5 to 10 percent of sodium silicate of an $Na_2O:SiO_2$ ratio of from 1:2 to 1:3, the fluorescent brightener is a mixture of brighteners intended for use on cotton and synthetic fabrics, the proportion of greenish blue dye is from 0.001 to 0.003 percent and the proportion of reddish blue dye is from 0.0003 to 0.001 percent, the composition contains from 25 to 50 percent of sodium sulfate and the particle sizes are such that no particles are larger than the opening of a No. 8 U.S. Standard Sieve Series sieve and no more than 10 percent pass through a No. 100 sieve.

8. A method of making a synthetic organic detergent composition for increasing the whiteness of fabrics which comprises making an alkaline crutcher mix containing from 30 to 70 percent of normally solid materials capable of being spray dried and less than 0.01 percent of a mixture of compatible blue dyestuffs in an aqueous medium and drying the described composition to solid particles in the 6 to 160 mesh range which are substantially white in color or of a color different from that of the blue dyestuffs, said solid particles comprising 5 to 85 percent, based on the weight of the dried composition, of a synthetic organic detergent or mixture of such detergents selected from the group consisting of anionic, nonionic and amphoteric detergents and 15 to 95 percent, based on the weight of the dried composition, of compounds selected from the group consisting of builder(s), filler(s), and adjuvant(s), and said dyestuffs being water soluble dyes of such different shades as to independently color fabrics washed therewith greenish blue and reddish blue, respectively, each of which dyes is substantially bleachable with aqueous hypochlorite bleach and contains in its structure a plurality of nuclear radicals selected from the group consisting of substituted and unsubstituted cyclohexyl, phenyl, naphthyl, anthracenyl and anthraquinonyl, at least one of which is substituted with a sulfonic acid or metal sulfonate group and at least one of which is linked to another nuclear radical of the described class by an azo or amino group, the remaining linking groups between nuclear radicals of the described group being selected from the group consisting of amino, azo, $-NHSO_2-$ and direct carbon to carbon bond, said dyes being substantive to fabrics and of substantially the same substantivity to cotton, said dye mixture being present in an amount to constitute from 0.0005 to 0.01 percent of the dried composition with the ratio of dyes within the dye mixture being within the range of 1:5 to 5:1, which proportion is such as to produce a fabric which, after washing in aqueous medium with said dried composition, is of an improved whiteness and a slightly blue tint, which tint is bluer than the color of fabrics washed with the composition absent the dye mixture.

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