ENHANCING THE APPARENT WHITENESS OF FABRICS BY APPLYING AN EFFECTIVE AMOUNT OF AN ALKALI AND HEAT STABLE WATER-SOLUBLE DISAZO BLUE DYESTUFF, FABRIC SOFTENING AND DETERGENT COMPOSITION THEREFOR

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References Cited

UNITED STATES PATENTS

2,424,778 5/1944 Tainsh ........................................ 8/77
3,254,046 5/1966 Marzolini et al. .............................. 8/77 X
3,083,166 3/1963 Harding .................................. 252/8.75 X
2,668,785 4/1950 Jefferson et al. .......................... 252/8.75 X

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ABSTRACT

The apparent whiteness of fabrics is enhanced by a method of treating the fabrics with an effective amount of an alkali and heat stable water-soluble disazo dyestuff using a sulfonated disazo dyestuff of the diphenyl, dinaphthyl type. A fabric softening and laundry detergent composition are disclosed therefor.

17 Claims, No Drawings
ENHANCING THE APPARENT WHITENESS OF FABRICS BY APPLYING AN EFFECTIVE AMOUNT OF AN ALKALI AND HEAT STABLE WATER-SOLUBLE DISAZO BLUE DYESTUFF, FABRIC SOFTENING AND DETERGENT COMPOSITION THEREFORE

This invention relates to compositions for, and a method of, enhancing the apparent whiteness of fabrics by treating the fabrics with a disazo dyestuff, and more particularly to the use of a sulfonated disazo dyestuff of the diphenyl, dinaphthyl type.

It has been found that the use of alkali and heat stable, water-soluble disazo blue dyes in relatively small amounts makes it possible to enhance the apparent whiteness of fabrics regardless of when it is applied. It is possible to use these materials either as an after rinse, in a fabric softener, in a pre-soak, or when used in combination with a liquid or solid detergent composition. The such compounds of the invention are so effective that, when used in combination with other materials such as in a laundering composition, there need not be so much dyestuff used that the composition itself becomes colored. In fact, many particulate laundry detergents appear to be even whiter with these color materials than when they are omitted. Furthermore, the use of such small quantities of bluing agent can be used that it becomes economically desirable to incorporate the material into ordinary laundry detergent compositions.

The use of the bluing agents heretofore known in the art has often resulted in an undesirable build-up of blue color on the fabrics treated in those instances where the compositions have been repeatedly applied over a period of time. The resulting residual color is not considered desirable. It has been discovered that any residual color that is imparted by the compounds of the invention can readily be removed simply by bleaching the fabrics with commonly used bleaching compositions. The fabrics can then again be treated with a disazo dye of the invention to provide desirable whitening.

The disazo blue dyestuffs of the invention are alkali and heat stable and water-soluble and are sulfonated with at least one and preferably two or more alkali metal sulfonate radicals. The compounds will also preferably contain two naphthyl rings and two phenyl rings. Highly desirable disazo dyestuffs are those of the phenyl-azo-naphthyl-azo-phenyl type and the phenyl-azo-naphthyl-azo-naphthyl type. Such compounds will preferably have the following structural formulas:

$$\text{R}_1 \text{R}_2 \text{R}_3 \text{R}_4 \text{N}=\text{N} \text{SO}_3\text{HCH}_3 \text{SO}_3\text{M} \text{NHCH}_3 \text{SO}_3\text{M} \text{SO}_3\text{HCH}_3$$

and

$$\text{R}_1 \text{R}_2 \text{R}_3 \text{R}_4 \text{N}=\text{N} \text{SO}_3\text{HCH}_3 \text{SO}_3\text{M} \text{NHCH}_3 \text{SO}_3\text{M} \text{SO}_3\text{HCH}_3$$

and include compounds having such formulas themselves and the metal complexes (for example the copper, nickel and cobalt complexes) of those compounds. In the above formulas each of $\text{R}_1, \text{R}_2, \text{R}_3, \text{R}_4$ and $\text{R}_5$ represents a moiety selected from the group consisting of hydrogen, halogen, hydroxyl, lower alkoxy of 1-3 carbon atoms and lower alkylox of 1-3 carbon atoms, $\text{M}$ is an alkali or alkaline earth metal, such as sodium, potassium, calcium, magnesium or the like (with sodium being the preferred cation) and $\text{A}$ is $\text{NH}, \text{NHCO-NH},$ or $\text{NH}_2\text{NH}$.

A highly desirable specific disazo dyestuff of the phenyl-azo-naphthyl-azo-naphthyl type is C.I. Acid Blue 113 which has the structural formula:

$$\text{NaO}_{2\beta} \text{N}=\text{N} \text{N}=\text{N} \text{NH} \text{SO}_3\text{Na}$$

A specific dyestuff material of the phenyl-azo-naphthyl-azo-phenyl type is the bis-copper complex of

$$\text{CH}_2\text{NH}:\text{O}_8 \text{N}=\text{N} \text{N}=\text{N} \text{NH} \text{SO}_3\text{Na} \text{SO}_3\text{Na}$$

which is formed by the reaction of 2 moles of 2-amino-N-methyl, 1-phenol-4-sulfonamide with 1 mole of 6,6'-iminobis-1-naphthal-3-sulfonic acid and converted to the bis-copper complex by treatment with ammoniacal copper sulfate. This compound is known as C.I. Direct Violet 48 and is sold as Sirius Supra Violet BL by Versona Dyestuff.

Mixtures of the blue dyestuffs disclosed herein can also be used, an especially desirable mixture being the mixture of C.I. Acid Blue 113 and C.I. Direct Violet 48 in a ratio of 9:1 to 1:9.

In a preferred embodiment of this invention it is contemplated that the blue disazo dyestuffs disclosed herein will be incorporated into a laundering composi-
tion containing an active detergent which may be a water-soluble alkali metal soap or other anionic, nonionic, amphoteric, zwiterionic, polar nonionic, or cationic detergents, or a mixture of two or more of the foregoing types of detergents.

The compatible anionic surface active agents include those surface active or detergent compounds which contain an organic hydrophobic group containing generally 8 to 26 carbon atoms and preferably 10 to 18 carbon atoms in their molecular structure, and at least one water-solubilizing group selected from the group of sulfonate, sulfate, carboxylate, phosphonate and phosphate so as to form a water-soluble detergent.

Examples of suitable anionic detergents which fall within the scope of the anionic detergent class include the water-soluble salts, e.g., the sodium, ammonium, and alkylolammonium salts, of higher fatty acids or resin salts containing about 8 to 20 carbon atoms, preferably 10 to 18 carbon atoms. Suitable fatty acids can be obtained from oils and waxes of animal or vegetable origin, e.g., tallow, grease, coconut oil, tall oil and mixtures thereof. Particularly useful are the sodium and potassium salts of the fatty acid mixtures derived from coconut oil and tallow, e.g., sodium coconut soap and potassium tallow soap.

The anionic class of detergents also includes the water-soluble sulfated and sulfonated synthetic detergents having an alkyl radical of 8 to 26, and preferably about 12 to 22 carbon atoms, in their molecular structure. (The term alkyl includes the alkyl portion of higher acyl radicals.)

Examples of sulfonated anionic detergents include higher alkyl aromatic sulfonates such as the higher alkyl benzene sulfonates containing from 10 to 16 carbon atoms in the higher alkyl group in a straight or branched chain, e.g., the sodium, potassium and ammonium salts of higher alkyl benzene sulfonates, higher alkyl toluene sulfonates, higher alkyl phenol sulfonates, and higher naphthalene sulfonates. A preferred sulfonate is linear alkyl benzene sulfonate having a high content of 3- (or higher) phenyl isomers and a correspondingly low content (well below 50 per cent) of 2- (or lower) phenyl isomers, i.e., wherein the benzene ring is preferably attached in large part at the 3 or higher (e.g., 4, 5, 6 or 7) position of the alkyl group and the counterion isomer in which the benzene ring is attached at the 2 or 1 position is correspondingly low. Particularly preferred materials are set forth in U.S. Pat. No. 3,320,174.

Other suitable anionic detergents are the olefin sulfonates, including long-chain alkene sulfonates, long-chain hydroxylkane sulfonates or mixtures of alkene-sulfonates and hydroxylkane-sulfonates. These olefin sulfonate detergents may be prepared in a known manner by the reaction of SO₂ with long-chain olefins containing 8 to 25, preferably 12-21, carbon atoms and having the formula RCH=CHR, where R is a higher alkyl group of 6 to 23 carbons and R', is an alkyl group of 1 to 17 carbons or hydrogen to form a mixture of sulfoines and alkene-sulfonic acids which is then treated to convert the sulfoines to sulfonates.

Further examples of sulfite or sulfonate detergents are paraffin sulfonates containing about 10-20, preferably about 15-20, carbon atoms, e.g., the primary paraffin sulfonates made by reacting long-chain alpha olefins and bisulfites and paraffin sulfonates having the sulfonate groups distributed along the paraffin chain as shown in U.S. Pat. Nos. 2,503,280; 2,507,088; 3,260,741; 3,372,188 and German Pat. No. 735,096; sodium and potassium sulfates of higher alcohols containing 8 to 18 carbon atoms such as sodium lauryl sulfate and sodium tallow alcohol sulfate; sodium and potassium salts of alpha-sulfonate acid esters containing about 10 to 20 carbon atoms in the acyl group, e.g., methyl alpha-sulfonate and methyl alpha-sulfonatoammonium, ammonium sulfates of mono- or diglycerides of higher (C₁₆-C₂₀) fatty acids, e.g., stearic monoglyceride monoammonium, and alkylammonium salts of alkyl polyelectrolyte ether sulfates produced by condensing 1 to 5 moles of ethylene oxide with one mole of higher (C₁₆-C₂₀) alcohol; sodium higher alkyl (C₆-C₈) glyceryl ether sulfonates; and sodium or potassium alkyl phenol polyelectrolyte ether sulfates with about 1 to 6 oxyethylene groups per molecule and in which the alkyl radicals contain about 8 to about 12 carbon atoms.

Paraffin sulfonates useful in the present invention are usually mixed secondary alkyl sulfonates having from 10 to 20 carbon atoms per molecule, preferably they will have at least 80 percent, usually at least 90 percent, of from 10-17 carbon atoms per molecule. Where the major proportion has 14-15 carbon atoms per molecule, optimum foaming performance appears to be obtained at varying concentrations and water hardnesses.

These sulfonates are preferably prepared by subjecting a cut of paraffin, corresponding to the chain lengths specified above, to the action of sulfur dioxide and oxygen in accordance with the then known sulfonation process. The product of this reaction is a secondary sulfonic acid which is then neutralized with a suitable base to provide the water soluble secondary alkyl sulfonate for use in the present invention. Similar useful secondary alkyl sulfonate may be obtained by other methods, e.g., by the sulfochlorination method in which chlorine and sulfur dioxide are reacted with paraffins in the presence of acetic light, the resulting sulfuryl chlorides being hydrolyzed and neutralized to form the secondary alkyl sulfonates. These compounds are particularly useful in heavy duty liquid detergent formulations containing the bluing agents of the invention.

The suitable anionic detergents include also the C₆-C₁₈ acrylic sarcosinates (e.g., sodium lauroyl sarcosinate), sodium and potassium salts of the reaction product of higher fatty acids containing 8 to 18 carbon atoms in the molecule esterified with isethionic acid, and sodium and potassium salts of the C₈-C₁₈ acyl N-methyl taurides, e.g., sodium cocoyl methyl taurate and potassium stearoyl methyl taurate.

Anionic phosphate surfactants in which the anionic solubilizing group attached to the hydrophobic group is an oxyacid of phosphorus are also useful in the detergent compositions. Suitable phosphate surfactants are the sodium potassium and ammonium alkyl phosphosphate esters such as (R-O)₉PO₃M and ROPO₃M₄ in which R represents an alkyl chain containing from about 8 to about 20 carbon atoms or an alkyl phenyl group having 8 to 20 carbon atoms and M represents a soluble cation. The compounds formed by including about one to 40 moles of ethylene oxide in the foregoing esters, e.g., [R-O(EO)n]PO₃M₄, are also satisfactory.

The particular anionic detergent salt will be suitably selected depending upon the particular formulation and the proportions therein. Suitable salts include the ammonium, substituted ammonium (mono-, di- and triethanolammonium), alkali metal (such as sodium and potassium) and alkaline earth metal (such as calcium and magnesium) salts of the higher alkyl benzene
sulfonates, olefin sulfonates, higher alkyl sulfates, higher fatty acid monoglyceride sulfates, and higher acyl sarcosinates. Particularly desirable salts of this type include the ammonium, triethanolammonium, sodium and potassium salts of the higher alkyl sulfates and the C10-C18 acyl sarcosinates.

The nonionic synthetic organic detergents are generally the condensation product of an organic aliphatic or alkyl aromatic hydrophobic compound and hydrophilic alkylene oxide groups. Practically any hydrophobic compound having a carboxy, hydroxy, amido, or amino group with a free hydrogen attached to the nitrogen can be condensed with an alkylene oxide such as ethylene oxide or with the polyhydration products thereof, e.g., polyethylene glycol, to form a nonionic detergent. Further, the length of the polyalkyleneoxy chain can be adjusted to achieve the desired balance between the hydrophobic and hydrophilic elements.

Useful for the nonionic compound types of hydrophobes are higher aliphatic alcohols and alkyl phenols, although others may be used such as carboxylic acids, carboxamides, mercaptans, sulphonamides, etc. The ethylene oxide condensates with higher-alkyl phenols represent a preferred class of nonionic compounds. Usually the hydrophobic moiety should contain at least about 6 carbon atoms, and preferably at least about 8 carbon atoms, and may contain as many as about 50 carbon atoms or more. The amount of alkylene oxide will vary considerably depending upon the hydrophobe, but as a general guide and rule, at least about 5 moles of alkylene oxide per mole of hydrophobe should be used. The upper limit of alkylene oxide will vary, also, but no particular criticality can be ascribed thereto. As much as 200 or more moles of alkylene oxide per mole of hydrophobe may be employed. While ethylene oxide is the preferred and predominating oxyalkylating reagent, other lower alkylene oxides such as propylene oxide, butylene oxide, and the like may also be used or substituted in part for the ethylene oxide.

Other nonionic compounds which are suitable are the polyoxyalkylene esters of the organic acids such as the higher fatty acids, the rosin acids, tall oil acids, acids from petroleum oxidation products, etc. These esters will usually contain from about 10 to about 22 carbon atoms in the acid moiety and from about 12 to about 30 moles of ethylene oxide or its equivalent.

Still other nonionic surfactants are the alkylene oxide condensates with the higher fatty acid amides. The fatty acid group will generally contain from about 8 to about 22 carbon atoms and this will be condensed with about 10 to about 50 moles of ethylene oxide. The corresponding carboxamides and sulphonamides may also be used as substantial equivalents.

Still another class of nonionic products are the oxyalkylated higher aliphatic alcohols. The fatty alcohols should contain at least 6 carbon atoms, and preferably at least about 8 carbon atoms. The most preferred alcohols are lauryl, myristyl, cetyl, stearyl and oleyl alcohols and the said alcohols should be condensed with at least about 6 moles of ethylene oxide and, preferably, about 10 to 30 moles of ethylene oxide. A typical nonionic product is oleyl alcohol condensed with 15 moles of ethylene oxide. The corresponding alkyl mercaptans when condensed with ethylene oxide are also admirably suitable in the compositions of the present invention.

Still other suitable nonionics are the polyoxyethylene polyoxypropylene adducts of 1-butanol. The hydrophobe of these nonionics has a minimum molecular weight of 1,000 and consists of an aliphatic monohydric alcohol containing from 1 to 8 carbon atoms to which is attached a heteric chain of oxyethylene and oxypropylene. The weight ratio of oxypropylene to oxyethylene covers the range of 95.5 to 85.15. Attached to this is the hydrophilic polyoxyethylene chain which is from 44.4 to 54.6 per cent of the total molecular weight of 1,400 to 4,000.

A particularly useful group of nonionics is marketed under the trade name "Pluronic." The compounds are formed by condensing ethylene oxide with a hydrophobic base formed by the condensation of propylene oxide with propylene glycol. The molecular weight of the hydrophilic portion of the molecule is of the order of 950 to 4,000 preferably 1,200 to 2,500. The addition of polyoxyethylene radicals to the hydrophobic portion tends to increase the solubility of the molecule as a whole. The molecular weight of the block copolymers varies from 1,100 to 15,000 and the polyethylene oxide content may comprise 20 to 80 per cent by weight.

Suitable nonionics may be derived by the condensation of ethylene oxide with the product resulting from the reaction of propylene oxide and ethylene diamine. The molecular weight varies from 500 to 4,500.

Other nonionic detergents include the ethylene oxide addends of monooesters of hexahydric alcohols and inner ethers thereof with higher fatty acids containing about 10 to 20 carbon atoms, e.g., sorbitan monolaurate, sorbitan mono-oleate, and mannitan monopalmitate.

The amphoteric detergents which can be used in the compositions of this invention are generally water-soluble salts of derivatives of aliphatic amines which contain at least one cationic group, e.g., non-quaternary nitrogen, quaternary ammonium, or quaternary phosphonium group, at least one alkyl group of about 8 to 18 carbon atoms and an anionic water-solubilizing carboxyl, sulfu, sulfato, phosphato or phophono group in their molecular structure. The alkyl group may be straight chain or branched and the specific cationic atom may be part of a heterocyclic ring.

Examples of suitable amphoteric detergents include the alkyl beta-amino-propionate, RN(H)C2H2COOM; the alkyl betaminodipropionate, RN(CH2)2COOM; the alkyl and hydroxy alkyl taurinates, RN(CH2)2CHSO4M; and the long-chain imidazole derivatives having the following formulas:

(I)

\[
\begin{align*}
\text{CH}_2 & \quad \text{N} \\
\text{CH}_2 & \quad \text{N}
\end{align*}
\]

(II)

\[
\begin{align*}
\text{CH}_2 & \quad \text{N} \\
\text{CH}_2 & \quad \text{N}
\end{align*}
\]

wherein R is an acyclic group of about 7 to 17 carbon atoms, W is selected from the group of ROH, R2COOM, and R3OR2COOM. Y is selected from the group consisting of OH-, RO-, R2SO4-, R3. R is an alkyl or hydroxyalkylene group containing 1 to 4 carbon atoms, R is selected from the group consisting of alkyl, alkyl aryl and fatty acyl glyceride groups having 6 to 18 carbon atoms in the alkyl or an acyl group; and M is a water-soluble cation, e.g., sodium potassium, ammonium or alkylolammonium.

Formula I detergents are disclosed in Volume II of "Surface Active Agents and Detergents" and in French Pat. No. 1,412,921 and Formula II detergents are de-
scribed in U.S. Pat. No. 2,773,068; U.S. Pat. No. 2,781,354; and U.S. Pat. No. 2,781,357. The acyclic groups may be derived from coconut oil fatty acids (a mixture of fatty acids containing 8 to 18 carbon atoms), lauric fatty acid, and oleic fatty acid and the preferred groups are C_{12}-C_{18} alkyl groups. Preferred detergents of this type are sodium N-lauryl beta-aminopropane, disodium N-lauryl iminodipropionate, and the disodium salt of 2-lauryl-cyclohexyl-1-hydroxy, 1-ethoxyethanoic acid, 1-ethanoic acid.

Zwitterionic detergents such as the betaines and sulfobetaines having the following formula are also useful:

\[
\begin{align*}
\text{R}_1 \quad & \quad \text{N}^{(\text{\text{\O}})} + \text{R}_2 - \text{R}_3 - \text{X} = \text{O} \\
\end{align*}
\]

wherein \( \text{R}_1 \) is an alkyl group containing about 10 to 18 carbon atoms, \( \text{R}_2 \) and \( \text{R}_3 \) are each \( \text{C}_{10}-\text{C}_{18} \) alkyl, \( \text{R}_1 \) is an alkyloxalkylalkylene group containing about 1 to 4 carbon atoms, and \( X = \text{C} \text{ or S} - \text{O} \). The alkyl group can contain one or more intermediate linkages such as amido, either or polyether linkages or non-functional substituents such as hydroxyl or halogen which do not substantially affect the hydrophobic character of the group. When \( X = \text{C} \), the detergent is called a betaine; and when \( X = \text{S} - \text{O} \), the detergent is called a sulfobetaine or sulfinate. Preferred betaine and sulfobetaine detergents are 1-(lauryl dimethylammonio) acetate, 1-(methyl dimethylammonio) propene-3-sulfonate, and 1-(methyl dimethylammonio) 2-hydroxypropene-3-sulfonate.

The polar nonionic detergents are those in which the hydrophilic group contains a semi-polar bond directly between two atoms, for example, \( \text{N} - \text{O} \); \( \text{P} - \text{O} \); \( \text{As} - \text{O} \); and \( \text{S} - \text{O} \). There is charge separation between the two directly bonded atoms, but the detergent molecule bears no net charge and does not dissociate into ions.

The polar nonionic detergents of this invention include open-chain aliphatic amine oxides of the general formula \( \text{R}_1 \text{R}_2 \text{R}_3 \text{N} - \text{O} \). For the purpose of this invention, \( R_1 \) is an alkyl, alkaryl, or monohydroxyalkyl radical having about 10 to 20 carbon atoms, \( R_2 \) and \( R_3 \) are each selected from the group consisting of methyl, ethyl, propyl, ethanol, and propanol radicals.

Other operable polar nonionic detergents are the open-chain aliphatic phosphine oxides having the general formula \( \text{R}_1 \text{R}_2 \text{R}_3 \text{P} - \text{O} \) wherein \( R_1 \) is an alkyl, alkenyl, or monohydroxyalkyl radical ranging in chain length from 10 to 18 carbon atoms, and \( R_2 \) and \( R_3 \) are each alkyl and monohydroxyalkyl radicals containing from 1 to 3 carbon atoms.

Cationic surface active agents may also be employed. Such agents are those surface active detergent compounds which contain an organic hydrophobic group and a cationic solubilizing group. Typical cationic solubilizing groups are amine and quaternary groups.

Examples of suitable synthetic cationic detergents are normal primary amines \( \text{RNH}_2 \) wherein \( R = \text{C}_{12}-\text{C}_{18} \); the diamines such as those of the type \( \text{RNH}_2 \text{CH}_2 \text{NH}_2 \) wherein \( R \) is an alkyl group of about 12 to 22 carbon atoms, such as N-2-aminoethoxy stearyl amine and N-2-aminoethoxymethyl amine; amide-linked amines such as those of the type \( \text{RNHCONHCH}_2 \text{NH} \) wherein \( R \) is an alkyl group of about 8 to 20 carbon atoms, such as N-2-amino ethyl-stearyl amide and N-amine ethylmyristyl amide; quaternary ammonium compounds wherein typically one of the groups linked to the nitrogen atom is an alkyl group of about 8 to 22 carbon atoms and three of the groups linked to the nitrogen atom are alkyl groups which contain 1 to 3 carbon atoms, including alkyl groups bearing inert substituents, such as phenyl groups, and there is present an anion such as halogen, acetate, methosulfate, etc. The alkyl group may contain intermediate linkages such as amido which do not substantially affect the hydrophobic character of the group, e.g., stearyl amido propyl quaternary ammonium chloride. Typical quaternary ammonium detergents are ethyl-dimethyl-stearyl ammonium chloride, benzylidimethyl-stearyl ammonium chloride, trimethyl-stearyl ammonium chloride, trimethyl-cetyl ammonium bromide, dimethyl-ethyl-lauryl ammonium chloride, dimethyl-propyl-myristil ammonium chloride, and the corresponding methosulfates and acetates.

The concentration of water-soluble organic detergent in the detergent compositions of the invention varies with the nature and form of the product, that is, usually from about 5 to 95 per cent by weight of detergent can be used. Preferably 8 to 35 per cent by weight is used in solid products, such as spray-dried powders; soap based products will normally contain 30–95 and preferably 50–90 per cent of soap, and from 5 to 30 per cent, preferably 8 to 20 per cent, by weight of detergent is used in liquid products.

Builder salts useful in the detergent formulations of the invention may be of any type well known in the detergent art generally and may be any suitable water-soluble, organic or inorganic builder salt. Useful builder salts include salts of alkali metal, alkaline earth metal, or heavy metals or combinations thereof. Ammonium or an ethanolammonium salt in a suitable amount may be added also, but generally, the sodium, potassium, or similar salts are preferred.

Preferred inorganic hydratable builder salts are the alkali metal polyphosphate salts which have the property of inhibiting precipitation of calcium and magnesium material in aqueous solution and of contributing to the heavy-duty performance of the detergent product. They may be considered as derived from orthophosphoric acid or the like by the removal of molecularly-bound water, though suitable means of manufacture may be employed if desired. Such complex or molecularly dehydrated polyphosphate salts may be used in the form of the normal or completely neutralized salt, e.g., pentapotassium tripolyphosphate, pentasodium tripolyphosphate, and potassium acid tripolyphosphate. The alkali metal salts of tetraposphoric acid may be used also. The alkali metal polyphosphate salts may be used in either anhydrous form or partially hydrated form.

Typical examples of hydratable organic builder salts which may be employed alone or in the aforementioned admixtures include the water-soluble aminopolycarboxylates such as the trisodium salt of nitrotriacetic acid and the di-, tri-, and tetrasodium salts of ethylene-diamine tetraacetic acid.

Other hydratable alkaline builder salts may be employed also, such as the soluble alkali metal borates, sulfates, carbonates, bicarbonates and silicates. Suitable silicates are sodium silicates having an Na₂O to SiO₂ ratio of 1.2:3.5, 1:2:5, 1:3.2 and so forth. Other suitable materials include citrates, diglycolates, nitrates chlorides, perborates and percarbonates.

Mixtures of two or more inorganic or organic salts can be used, as can mixtures of inorganic salts with organic salts. The proportion of builder salts is preferably, for example, in the range of about 1 to 20 parts per part of the active detergent.

Various other materials may be added in suitable
amounts. Materials such as the higher fatty acids amides may be added to improve detergent and modify the foaming properties in a desirable manner. Examples thereof are the higher fatty acid alkanolamides, preferably having 2-3 carbons in each alkanol group and a fatty acyl radical within the range of 10-18 carbons, preferably 10-14 carbons, such as lauric or myristic monoethanolamides, diethanolamides and iso-propionamides. Tertiary higher alkyl amine oxides such as having about 10-18 carbons in one alkyl group, e.g., lauryl or myristyl dimethylamine oxide, may be added also. Fatty alcohols of 10-18 carbons such as lauryl or coconut fatty alcohols, or cetyl alcohol are suitable additives also. A hydrotrropic material such as the lower alkyl aryl sulfonates, e.g., sodium toluene- or xylene-sulfonates, also can assist processing. In general, these materials are added in minor amounts, usually from about 1/2 to 10 percent, preferably 1 to 6 percent based on the total solids.

The mixtures may also contain optical brightening agents or fluorescent dyes (e.g., in amounts in the range of about 1/20 to 3 percent); germicidal ingredients such as halogenated carbanilides, tri-chlorocarbanilide, halogenated salicylanilide, tri-bromosalicylanilide, halogenated bis-phenols, e.g., hexachlorophene; halogenated trifluoromethylphenyl urea; the zinc salt of 1-hydroxy-2-pyrimidethione and the like (e.g., in amounts in the range of about 1/50 to 2 percent).

Soil-suspending agents can also be included. These are generally water-soluble or hydrophilic polymeric substances such as the lower alkyl cellulose ethers, e.g., methyl cellulose and ethyl cellulose, hydroxyalkyl cellulose ethers, e.g., hydroxyethyl cellulose, cellulose ethane sulfonic acid, cellulose glycolic acid, carboxy lower alkyl cellulose compounds, e.g., sodium carboxy methyl cellulose, potassium carboxy methyl cellulose, sodium carboxy ethyl cellulose, sodium carboxy propyl cellulose, and the like, water-soluble or dispersible synthetic polymeric materials which may be homopolymers, copolymers, graft copolymers, terpolymers, interpolymers, and the like and are illustrated by polyvinyl pyrrolidone, polyvinyl alcohol, hydrolyzed polyvinyl acetate, polyacrylic acid, polyacrylamide, maleic anhydride copolymers with alkyl vinyl ethers, e.g., methyl vinyl ether, natural products such as starch, and the like. These agents generally present in an amount, for example, in the range of about 1/20 to 6 percent.

Other additives include antioxidants such as 2,6-di-tertbutylphenol, or other phenolic antioxidant material (e.g., in amounts in the range of about 0.001 to 0.1 percent); bleaching agents; corrosion inhibitors; sequentants, e.g., ethylene diamine tetraacetic acid, sodium gluconate, and the like; alcohols to improve the compatibility of the various components such as ethanol, propanol and isopropanol; tarnish inhibitors such as ethylene thiourea; perfumes; and thickening agents.

As stated above, the bluing agents are useful when applied from presoak products as well as from regular laundry detergent compositions. Presoak products are similar to the laundry detergent compositions and generally contain a surface active agent and a builder salt such as those described above. The presoak product also often will contain an enzyme of the proteolytic type (e.g., pepsin, subtilisin, trypsin, papain, bromelin, and the like). The surface active agent is typically present in an amount of 3-95 percent by weight of the presoak composition, preferably about 5-25 percent by weight. Generally the builder salt, when present is employed in the amount of 30-90 percent by weight, and, when included, the enzyme is present in amounts of 0.001 to 4.0 percent preferably 0.05 to 2.0 percent by weight. As in the use of the ordinary laundry detergent various other additives can be included to alter or enhance the effectiveness and the esthetics of the composition.

The bluing agents can also be applied to fabrics when incorporated into a fabric softener composition. Fabric softeners are of any suitable type known to have the desired conditioning effects. Thus, cationic, amphoteric, nonionic and anionic surface active agents are useful. Included in this group are the quaternary ammonium halides such as the mixed higher and lower alkyl ammonium chlorides and bromides wherein there are present one or two higher alkyls of 8 to 20 carbon atoms, preferably about 1 to 18 carbon atoms, and two or three lower alkyls of 1 to 4 carbon atoms, preferably of 1 or 2 carbon atoms. Instead of a higher alkyl radical an aryl alkyl radical such as benzyl may be used.

Each of the cationic compounds is distearyl dimethyl ammonium chloride, lauryl trimethyl ammonium bromide and stearyl dimethyl benzyl ammonium chloride. Also useful are various other cationics, such as alkyl pyridine salts, alkyl imidazolines, higher alkyl amines, of the primary, secondary, or tertiary types and higher alkyl guanidine salts, e.g., 1-methyl-1-stearylaminoethyl-2-stearyl imidazolinium methosulfate, 2-heptadecyl-1-methyl-(2-stearylamido)ethyl imidazolinium methyl sulfate, steary pyridinium halides, cetyl isoquinolinium bromide and alkyl morpholino chlorides. In the aforementioned cases, lower alkyl is of 1 to 5 carbon atoms, preferably 1 or 2, and higher alkyl is of about 8 to 20 carbon atoms, preferably 12 to 18.

Of the amphoteric materials those sold as Soromines, Deriphats, Miranols etc., are good conditioners. The Soromines, AL and AT, are complex fatty amido softeners which have been found to be excellent for the intended purpose. Of the nonionics, the preferred products are polyoxyethylene (4) lauryl ether, sold as Brij 30; myristyl dimethyl amine oxide, sold as Textamine Oxide TA; nonylphenoxynol polyoxyethylene, sold as Igepal CO-880; and polyoxyethylene sorbitan mono-stearyl, sold as Tween 61.

Among the anionic softeners the ones that are most useful are the water-soluble higher fatty acid soaps and the synthetic organic surface active agents of the sulfonate reaction type. The soaps include the alkali metal, amine, ammonium, and alkanolamine soaps. The higher fatty acids are of 8 to 20 carbon atoms, preferably mostly of 12 to 18 carbon atoms and are those that occur naturally in vegetable and animal oils and fats, usually in mixtures in triglycerides. The amines and alkanolamines are of lower alkyls and alkanolamines such as those of 1 to 4 carbon, preferably of 2 to 3 carbon atoms. The sulfuric reaction products are balanced compounds having lipophilic and hydrophilic groups, with the lipophile portion usually being a higher alkyl or alkyl aryl, e.g., alkyl phenyl wherein the alkyl is of 12 to 15 carbon atoms. The higher alkyls may be of 8 to 20 carbon atoms, preferably of 12 to 18. Alternatively, the lipophile portion may be made of polymerization of lower alkylene oxide(s) to a suitable chain length, usually of 10 to 40 oxyalkylene groups of 2 to 4 carbon atoms each. The lipophile balancing group, the hydrophilic moiety, will usually be a water-soluble
sulfate or sulfonate of an alkali metal, an alkaline earth metal, ammonium, amine or alkanolamine of the type previously described in conjunction with the nonionic softener exposition.

Lengthy descriptions of the softeners are not given herein because all such compounds are generally applicable to the present invention and are known to those of skill in the art. For example, descriptions of softeners can be found in the reference work \textit{Detergents and Emulsifiers 1969 Annual}, by John W. McCutcheon, wherein those surface active agents that are especially useful as softeners are so characterized. Also, see the text \textit{SYNTHETIC DETERGENTS}, by Schwartz, Perry and Berch, published in 1958 by Interscience Publishers.

Fabric softener compositions may also contain various adjuvants to impart desirable properties in addition to softening and bluing to the fabrics treated. Thus, they may contain bactericides, fungicides, fluorescent or optical brighteners, e.g., aminostilbenes, triazines, ozazoles, pyrazolines, etc., perfumes, deodorants and lubricants.

Still another method for applying the bluing agents of this invention to fabrics simply involves the addition of a premeasured amount of bluing agent in an aqueous medium to a given quantity of fabric to be bleached. Regardless of the method used, the disazo dye will normally be used in an amount by weight of the disazo blue dyestuff of not greater than 1.5 parts per million parts by weight of the fabric to be treated, and preferably will be less than 1.0 part per million. The lower limit on the amount of disazo blue dye to be added is that amount necessary to effectively whiten the fabrics. Generally at least about 0.03 part per million will be used, and preferably at least about 0.1 part per million is used. When incorporating the dyestuff into a conventional type solid particulate laundering composition in which approximately 100 grams of detergent will be employed for a single load, an amount of dyestuff not more than 0.005 percent by weight, based upon the weight of the detergent composition, will be employed, and desirably not more than 0.003 percent will be employed. Even smaller amounts are generally adequate. For example, when using the preferred C.I. Direct Violet 4B (C.I. 29125) the amount used will normally not exceed that amount necessary to equal 0.5 part per million parts of fabric (0.0015 percent of a conventional granular laundry detergent), and preferably only from 0.1 to 0.4 part per million is used. Accordingly, it will be seen that for a normal wash load it will only be necessary to utilize amounts of blue dye on the order of about 1/1000 of a gram. In formulating detergent compositions containing the disazo blue dyestuffs of the invention they may be added in the crutcher before spray drying of a spray-dried particulate detergent, or they may be mixed into the composition after spray drying or added at any other time during the formulation of the liquid detergents. They may also be post-added to the detergent composition either alone or on a suitable carrier. The compounds of the invention are both alkali and heat stable and therefore lend themselves to widely varied formulating techniques.

When used in a liquid detergent, a pre-soak, or a fabric softener composition the per cent of disazo dye used will be approximately twice the amount described above for use in a granular or spray-dried composition. This is because an amount by weight of roughly half of these compositions is used for a normal load of wash compared to the amount of granular detergent used. Thus, for example, a fabric softener composition may contain the disazo blue dye in an amount up to about 0.01% by weight.

The following examples are given to further illustrate the invention. In the examples as throughout the specification all parts or percentages given are by weight unless otherwise specified.

\textbf{EXAMPLE 1}

A spray-dried laundry detergent having the following composition was prepared:

<table>
<thead>
<tr>
<th>Amount (Wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Linear tridecyl benzene sulfonate</td>
</tr>
<tr>
<td>Neodol 45-11*</td>
</tr>
<tr>
<td>Sodium tripolyphosphate</td>
</tr>
<tr>
<td>Sodium Silicate (1:2.35 Na$_2$O:SiO$_2$)</td>
</tr>
<tr>
<td>Carboxymethyl cellulose</td>
</tr>
<tr>
<td>Optical brighteners</td>
</tr>
<tr>
<td>Polyvinyl alcohol</td>
</tr>
<tr>
<td>Sirius Supra Violet BL**</td>
</tr>
<tr>
<td>Water</td>
</tr>
<tr>
<td>Sodium sulfate</td>
</tr>
<tr>
<td>Perfume</td>
</tr>
</tbody>
</table>

*nonionic surface active agent which is a polyoxyethylated long chain alkanol, specifically the reaction product of 11 mols of ethylene oxide with one mol of a blend of 14 and 15 carbon atoms primary alkanols

**described hereinabove

The spray-dried product had a white color, a cup weight of about 80 grams and a density of about 0.35.

A plurality of swatches of cotton, Dacron, Arnel, Orlon, Creslan, nylon and blends of these fabrics together with cleaned cotton towels to form a full load (8 pounds) is washed in an automatic washing machine in ordinary tap water (New Brunswick, New Jersey hardness of about 100 PPM), containing approximately 100 grams of the spray-dried detergent composition equivalent to approximately 0.15 percent of detergent. The wash water temperature is 120°F. and has a pH of approximately 9.5. The washing is continued for 10 minutes after which the load is thoroughly rinsed in the same tap water at a temperature about 90°-100°F.

The resulting cleaned and whitened fabrics were evaluated against a similarly constituted batch of fabrics washed with a detergent composition that was the same except that it did not contain the Sirius Supra Violet BL. The evaluation was made by ten panelists under both incandescent light and north daylight. The panelists showed a strong preference for the fabrics that were washed in the composition containing Sirius Supra Violet BL.

The detergent composition itself was considerably whiter looking than a control without the bluing agent. Readings were taken of the detergent and the control on a Hunter D-25 Color Difference Meter and the detergent with the dyestuff was considerably less yellow. The results of the Difference Meter Readings are shown in the chart below wherein Rd is the Reflectance value, -a is the greenness indication, and +b is the yellowness indication.
EXAMPLE 2
A spray-dried composition similar to that described above was formulated using 0.002 percent of C.I. Acid Blue 113 instead of the Sirius Supra Violet BL (i.e., C.I. Direct Violet 48).

Again a detergent product was formed which had the ability to enhance the apparent whiteness of the fabrics treated.

EXAMPLE 3
A composition similar to that described in Example 1 above was formulated with the exception that the bluing agent constituted a mixture of 40 percent C.I. Direct Violet 48 and 60 percent C.I. Acid Blue 113. The total amount of blue dyestuff was 0.001 percent and the amount of sodium sulfate was reduced to compensate for the difference in the total amount of dyestuff used.

EXAMPLE 4
A spray-dried granular laundry detergent composition can be prepared from the following components:

<table>
<thead>
<tr>
<th>Component</th>
<th>Amount (Wt. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neodol 45-11</td>
<td>10.0</td>
</tr>
<tr>
<td>Sodium Carbonate</td>
<td>45.0</td>
</tr>
<tr>
<td>Sodium Silicate</td>
<td>18.4</td>
</tr>
<tr>
<td>Carboxymethyl cellulose</td>
<td>0.5</td>
</tr>
<tr>
<td>Brighteners</td>
<td>0.84</td>
</tr>
<tr>
<td>Water</td>
<td>10.0</td>
</tr>
<tr>
<td>C.I. Direct Violet 48</td>
<td>0.002</td>
</tr>
<tr>
<td>Sodium Sulfate</td>
<td>15.258</td>
</tr>
</tbody>
</table>

The spray-dried product had an 80 gram cup weight and a density of about 0.35.

A load comprising swatches of various fabrics washed in the same way as described above with respect to the fabrics of Example 1 is compared to a control batch. The fabrics treated with the control composition were considerably less white than those treated in accordance with the invention.

EXAMPLE 5
A spray-dried composition similar to that described in Example 4 was formulated using 0.001 percent of C.I. Direct Violet 48 instead of C.I. Acid Blue 113. A substantially white detergent product was obtained. The product clearly enhanced the apparent whiteness of the fabrics treated therewith.

EXAMPLE 6
A composition similar to that described in Examples 4 and 5 above was formulated with the exception that the bluing agent constituted a mixture of 60 percent C.I. Direct Violet 48 and 40 percent C.I. Acid Blue 113. The total amount of blue dyestuff was 0.001 percent.

EXAMPLE 7
A spray-dried laundry composition was formed having the following composition:

<table>
<thead>
<tr>
<th>Component</th>
<th>Amount (Wt. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Linear Tridecyl benzene sulfonate</td>
<td>10.0</td>
</tr>
<tr>
<td>Primary C_{17-18} Alcohol with 11 mols ethylene oxide</td>
<td>2.0</td>
</tr>
<tr>
<td>Sodium Soap of a mixture of tallow and fatty acids</td>
<td>2.0</td>
</tr>
<tr>
<td>Sodium Triphosphate</td>
<td>45.0</td>
</tr>
</tbody>
</table>

EXAMPLE 8
A product similar to that described in Example 7 above was formulated except that an equivalent amount of C.I. Direct Violet 48 was substituted for the C.I. Acid Blue 113. The resulting product was equally efficacious in enhancing the visual whiteness of test towels.

EXAMPLE 9
A composition similar to that described in Example 7 above was formulated using a detergent having the same composition described therein but wherein the cup weight was 140 grams rather than 80 grams and the amount of C.I. Acid Blue 113 used was sufficient to form a laundry detergent composition containing 0.0013 percent of the dyestuff. A visual examination following a five wash bundle test showed that the composition containing the dye-stuff was again preferred over the control.

When the identical composition was similarly tested with one cup of about five per cent aqueous sodium hypochlorite bleach solution present, the effect of the dyestuff was eliminated and the product as compared to the control was close to parity. The results of the test are shown in the following table:

<table>
<thead>
<tr>
<th>PANEL REFERENCE (%)</th>
<th>Blue</th>
<th>Control</th>
<th>No pref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>No Bleach</td>
<td>66</td>
<td>23</td>
<td>11</td>
</tr>
<tr>
<td>With Bleach</td>
<td>41</td>
<td>50</td>
<td>9</td>
</tr>
</tbody>
</table>

EXAMPLE 10
A spray-dried detergent was formulated having the formula:

<table>
<thead>
<tr>
<th>Component</th>
<th>Amount (Wt. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Linear tridecyl benzene sulfonate</td>
<td>18.0</td>
</tr>
<tr>
<td>Sodium triphosphate</td>
<td>33.5</td>
</tr>
<tr>
<td>Sodium sulfate</td>
<td>29.5</td>
</tr>
<tr>
<td>Sodium silicate</td>
<td>7.0</td>
</tr>
<tr>
<td>Sodium tetraborate</td>
<td>1.0</td>
</tr>
<tr>
<td>Carboxymethyl cellulose</td>
<td>0.4</td>
</tr>
<tr>
<td>Polyniydi alcohol</td>
<td>0.2</td>
</tr>
<tr>
<td>C.I. Direct Violet 48</td>
<td>0.00075</td>
</tr>
<tr>
<td>Brighteners</td>
<td>0.71</td>
</tr>
<tr>
<td>Moisture</td>
<td>9.5</td>
</tr>
</tbody>
</table>

The above formulation was spray-dried with the C.I. Direct Violet 48 having been added in the crutcher prior to the spray-drying operation. The product pow-
A liquid laundry composition similar to that described in Example 12 was formulated using 0.003 percent of C.I. Acid Blue 113 instead of C.I. Direct Violet 48. Fabrics treated with the product made in accordance with the invention had enhanced apparent whiteness when compared to a control made without the disazo dye.

EXAMPLE 14

A composition similar to that described in Examples 12 and 13 above was formulated with the exception that the blueing agent constituted a mixture of 50 percent C.I. Direct Violet 48 and 50 percent C.I. Acid Blue 113. The total amount of blue dyestuff was 0.0025 percent. Fabrics treated with this composition also had improved apparent whiteness.

EXAMPLE 15

A fabric softener composition was formed having the following composition:

<table>
<thead>
<tr>
<th>Component</th>
<th>Amount (Wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-Heptadecyl-1-methyl-1</td>
<td>9.50 (7.1 A.I.)</td>
</tr>
<tr>
<td>[1-(2-Deoxyoctyloxy)methyl] imidazolium methyl sulfate, 75% A.I.</td>
<td>4.50</td>
</tr>
<tr>
<td>Benzyl Fast Blue 5R (C.I. Acid Blue 113)</td>
<td>0.50</td>
</tr>
<tr>
<td>Aqueous Brightener Solution, 23% A.I.</td>
<td>0.37</td>
</tr>
<tr>
<td>Perfume</td>
<td>0.30</td>
</tr>
<tr>
<td>Water</td>
<td>88.33</td>
</tr>
</tbody>
</table>

In a 5-wash clean load test, this composition was superior to a control composition in whiteness preference under three lights - incandescent, north daylight and fluorescent.

EXAMPLE 16

A laundry pre-soak composition was formulated from:

<table>
<thead>
<tr>
<th>Component</th>
<th>Amount (Wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Linear tridecyl benzene sulfonate</td>
<td>6.0</td>
</tr>
<tr>
<td>Sodium tripolyphosphate</td>
<td>7.0</td>
</tr>
<tr>
<td>Sodium sulfate</td>
<td>9.908</td>
</tr>
<tr>
<td>Sodium silicate</td>
<td>7.0</td>
</tr>
<tr>
<td>Benzyl Fast Blue 5R (C.I. Acid Blue 113)</td>
<td>0.002</td>
</tr>
<tr>
<td>Brighteners</td>
<td>0.33</td>
</tr>
<tr>
<td>Protease Enzyme (Alcalase, Novo)</td>
<td>0.76</td>
</tr>
<tr>
<td>Moisture</td>
<td>6.0</td>
</tr>
</tbody>
</table>

In clean load soak tests this composition was preferred over a control for whiteness on both terry cloth towels and diapers; on synthetic fabric swatches, the two products were similar in whiteness. We claim:

1. A method for enhancing the apparent whiteness of fabrics comprising applying thereto an effective amount up to 1.5 parts by weight per million parts of said fabric of an alkali and heat stable water-soluble disazo blue dyestuff containing at least one alkali metal sulfonate radical and selected from the group consisting of compounds having the formula
3,762,859

17 and those having the formula

\[
\text{R}_1 - \text{N} = \text{N} - \text{R}_2 \text{SO}_3\text{M}
\]

and the metal complexes thereof, and wherein each of \( \text{R}_1, \text{R}_2, \text{R}_3, \text{R}_4, \text{R}_5 \), and \( \text{R}_6 \) is selected from the group consisting of hydrogen, halogen, hydroxyl, lower alkoxy and lower alkyl groups; \( \text{M} \) is alkali or alkaline earth metal and \( \text{A} \) is NH, NH\text{CO-NH or NH-aryl-NH.}

2. Method of claim 1 wherein said disazo blue dye-stuff is of the diphenyl-dinaphthyl type.

3. A method in accordance with claim 1 wherein said disazo blue dye-stuff is present in an amount of from about 0.1 to 0.4 parts by weight per million parts by weight of said fabric.

4. A laundry detergent composition comprising an organic surface active compound selected from the group consisting of a water-soluble alkali metal soap, anionic, nonionic, amphoteric, zwitterionic, polar nonionic and cationic detergents and an effective amount of an alkali and heat stable water-soluble disazo blue dye-stuff containing at least one alkali metal sulfonate radical, said composition being adapted to be applied to substantially all commonly used fabrics whereby enhanced apparent whiteness thereof is obtained said dye-stuff being selected from the group consisting of compounds having the formula

\[
\text{R}_1 - \text{N} = \text{N} - \text{R}_2 \text{SO}_3\text{M}
\]

and those having the formula

\[
\text{R}_1 - \text{N} = \text{N} - \text{R}_2 \text{SO}_3\text{M}
\]

and the metal complexes thereof, and wherein each of \( \text{R}_1, \text{R}_2, \text{R}_3, \text{R}_4, \text{R}_5 \), and \( \text{R}_6 \) is selected from the group consisting of hydrogen, halogen, hydroxyl, lower alkoxy and lower alkyl groups; \( \text{M} \) is alkali or alkaline metal and \( \text{A} \) is NH, NH\text{CO-NH or NH-aryl-NH.}

5. A laundry detergent composition in accordance with claim 4 wherein said disazo blue dye-stuff is C.I. Direct Violet 48 (C.I. 29125).

6. A laundry detergent composition in accordance with claim 5 wherein said composition is a granular solid and said disazo dye-stuff is present in an amount of up to about 0.0015 per cent by weight based upon the weight of the total laundry detergent composition.

7. A laundry detergent composition in accordance with claim 4 wherein said disazo blue dye-stuff is C.I. Acid Blue 113 (C.I. 26360).

8. A laundry detergent composition in accordance with claim 4 wherein said disazo blue dye-stuff comprises a mixture of C.I. Acid Blue 113 (C.I. 26360) and C.I. Direct Violet 48 (C.I. 29125).

9. A laundry detergent composition in accordance with claim 4 wherein said composition is a granular solid and said disazo dye-stuff is present in an amount of up to about 0.005 per cent by weight based upon the weight of the total laundry detergent composition.

10. A laundry detergent composition in accordance with claim 4 wherein said composition is a granular solid and said disazo dye-stuff is present in an amount of up to about 0.003 per cent by weight based upon the weight of the total laundry detergent composition.

11. A laundry detergent composition in accordance with claim 4 wherein said composition is a heavy-duty liquid and said disazo blue dye-stuff is present in an amount of up to about 0.01 per cent by weight of said composition.

12. A laundry detergent in accordance with claim 4, wherein said surface active compound is selected from the group consisting of linear tridecyl benzene sulfonate, sodium soap of mixed tallow and coconut fatty acids and mixtures thereof.

13. A laundry detergent in accordance with claim 4, further containing water-soluble, organic or inorganic builder salt.

14. A laundry detergent in accordance with claim 13, wherein said builder is an alkali metal polyphosphate.

15. A laundry detergent in accordance with claim 13, wherein said builder is sodium silicate having an Na\text{2O to SiO}_3 ratio of at least 1.2.35.

16. A laundry detergent in accordance with claim 4, comprising from an effective amount up to 0.005 per cent by weight of disazo dye-stuff, from about 5 to 95 per cent by weight of organic surface active compound and from about 1 to 20 parts of builder per part of organic surface active compound said dye-stuff being selected from the group consisting of compounds having the formula

\[
\text{R}_1 - \text{N} = \text{N} - \text{R}_2 \text{SO}_3\text{M}
\]
17. A fabric softening composition comprising an organic surface active compound and an effective amount up to about 0.01 percent by weight of said composition of an alkali and heat stable water-soluble disazo blue dyestuff containing at least one alkali metal and the metal complexes thereof, and wherein each of R, R1, R3, R4, and R5 is selected from the group consisting of hydrogen, halogen, hydroxyl, lower alkoxy and lower alkyl groups; M is alkali or alkaline earth metal and A is NH, NH-CO-NH or NH-aryl-NH.

19. A fabric softening composition comprising an organic surface active compound and an effective amount up to about 0.01 percent by weight of said composition of an alkali and heat stable water-soluble disazo blue dyestuff containing at least one alkali metal sulfonate radical, said composition being adapted to be applied to all commonly used fabrics whereby enhanced apparent whiteness is obtained and wherein said dyestuff is selected from the group consisting of compounds having the formula

and those having the formula

and the metal complexes thereof, and wherein each of R, R1, R3, R4, and R5 is selected from the group consisting of hydrogen, halogen, hydroxyl, lower alkoxy and lower alkyl groups; M is alkali or alkaline earth metal and A is NH, NH-CO-NH or NH-aryl-NH.