

UNITED STATES PATENT OFFICE

2,189,807

WASHING OF DISCHARGE PRINTS

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No Drawing. Application March 26, 1937,
Serial No. 133,266

14 Claims. (Cl. 8—69)

This invention relates to the washing of textile materials, more particularly it relates to the washing of fabrics dyed with water-soluble dyes, still more particularly it relates to the washing of textile fabrics dyed with azo colors. In a more limited sense the invention pertains to discharge printing and to the washing of discharge prints of the white and colored type. In a preferred embodiment the invention relates to the washing of discharge prints on cotton and viscose rayon in which azo dyes are used in the ground shades. The invention also relates to washing solutions and to washing compositions.

Discharge prints are of two types: white, and colored. In preparing a discharge print, dyeings are first made of a color which can be reduced by the discharge agent. This dye, known as the "ground color," is usually of the azo type. In white discharge printing, the dyed goods are printed with a gum paste containing sodium sulfoxylate formaldehyde ($\text{Na}_2\text{SO}_2 \cdot \text{CH}_2\text{O} + 2\text{H}_2\text{O}$). The printed goods are aged in an atmosphere of steam at $100^\circ\text{--}105^\circ\text{C}$. for about five minutes. Under these conditions Na_2SO_2 is liberated and in turn acts to reduce the dye into amino- and hydroxyaromatic bodies. The print is washed to remove the products of the discharge, frequently quite yellow in color, and the discharge paste. In practice, the methods of washing vary widely, depending largely on the fastness of the ground color. The wash solution may vary from water alone, to a 0.5% solution of a detergent such as the fatty alcohol sulfates or soap. The temperatures may vary between room temperature and $160^\circ\text{--}180^\circ\text{F}$. The time may vary from a minute to a half hour. In all cases the conditions selected by the processor are the result of a compromise. As strong detergent action is used as is possible without removing appreciable quantities of the ground color. In practice, it is not unusual for 20% of the dye to be removed from the goods. This removal of dye is detrimental, not only because of loss of strength of the dyeing, but also because the dye removed into the bath shows a marked tendency to stain the discharged portions of the print.

In colored discharge printing, a dye which is applicable to the goods under the discharge conditions is incorporated, together with the sodium sulfoxylate formaldehyde in the printing paste. Vat colors are customarily used. Under the aging conditions outlined above, the discharged portion of the print is dyed by the reduced vat, and the vat dye becomes fixed on oxidation. A wash at 160°F . in a 0.5% solution of a fatty alcohol sul-

fate or soap is practised to develop the brightness of the vat color. Under such drastic detergent conditions, a considerable loss in strength of the best of the azo type of ground colors occurs, while many less fast colors cannot be used because of their failure to withstand this processing.

Dyed textile fabrics have been soaked in heavy metal salt solutions in an attempt to improve their fastness to subsequent washings. Aluminum, chromium, iron and tin salt solutions have been used successfully with some dyes. However, their limited success is offset by the fact that the treatment requires considerable handling of the goods which is not only time consuming but an economic loss. Magnesium and calcium salt solutions have been proposed for use in this connection but have not met with any success since they have little, if any, effect upon the wash fastness of water-soluble dyes.

We have found that if dyed textiles are washed with an aqueous solution containing water-soluble calcium and magnesium salts and a compatible detergent, very little color is removed. This discovery is surprising in view of the above fact that the pretreatment of dyed fabrics with aqueous solutions does not render them fast to subsequent washing steps. When one considers the large volume of washing steps in a print works or a commercial laundry, the importance of this discovery can be realized. The invention is of great importance in the washing of discharge prints where strong detergent and scouring agents are used at elevated temperatures.

This invention has as an object the washing of textile materials. A further object is the washing of textile fabrics dyed with water-soluble dyes. A still further object is the washing of textile prints dyed with azo dyes. A still further object is the washing of textile prints under such conditions that color is not removed. Other objects include the washing of discharge prints of dyeings of water-soluble colors on cotton and viscose rayon, the preparation of washing solutions and compositions, and a general advancement of the art. Still further objects will appear hereinafter.

The above and other objects are accomplished by the following invention which comprises washing textile, and more specifically dyed textile materials with an aqueous solution containing a water-soluble alkaline earth metal salt and a detergent compatible therewith. The alkaline earth metal salts are preferably water-soluble

calcium and magnesium metal salts such as calcium chloride and magnesium sulfate, and the detergent one which has good scouring properties. In a more limited sense the objects are accomplished by washing discharge patterns on dyeings of direct, after-treated and developed azo colors on cotton and viscose rayon with an aqueous solution containing a water-soluble calcium or magnesium salt and a water-soluble detergent selected from the class consisting of the higher aliphatic hydrocarbon sulfates and the water-soluble salts thereof, and the long chain aliphatic hydrocarbon betaine derivatives. These agents are characterized by being strong detergent and scouring agents.

By the term "higher" when referring to an aliphatic hydrocarbon radical is meant one containing an aliphatic chain of at least eight carbon atoms. The aliphatic hydrocarbon radicals may be saturated or unsaturated and may be substituted by other groups such as hydroxyl, and halogen such as chlorine groups. As specific examples of aliphatic hydrocarbon sulfates falling within the scope of this invention may be mentioned the water soluble salts of octyl, nonyl, decyl, dodecyl, tetradecyl, hexadecyl, octadecyl and 9, 10-octadecenyl sulfates and mixtures. Among the water soluble salts may be mentioned calcium, magnesium, sodium, potassium, ammonium and amine salts as well as the quaternary ammonium salts. Thus mono, di and tri methyl, ethyl, propyl, isopropyl, butyl, cyclohexyl, ethanol, propanol, etc. amines may be used as salt forming groups. Quaternary ammonium salts such as tetra ethyl-, tetramethyl-, triethylmethyl etc. dodecyl, octadecyl and hexadecyl sulfates are especially useful. Other specific compounds which are equivalents to those mentioned will be obvious to those skilled in the art.

Mixtures of sulfates such as those obtained by catalytic hydrogenation of the free fatty acids of coconut oil and sulfation of the entire mixture or fraction as well as those obtained from the sulfation of alcohols obtained by catalytic hydrogenation of palm kernel oil or the free fatty acids thereof and those obtained by sulfating alcohols obtained by saponifying spermaceti, sperm oil, beeswax and distilling are illustrative of suitable mixtures. These and other sulfates are described in Bertsch Patent 1,968,797.

As a general rule the neutralized sulfate products which are sold commercially contain an equivalent amount of free salt. Thus if the sodium salts are dissolved in water a considerable amount of sodium sulfate is present. We have eliminated listing the amount of sodium etc. sulfate present in the following tests for the most part in order that they be more clearly understood.

Among the operative betaine compounds may be mentioned those which contain a long aliphatic hydrocarbon chain, i. e. from eight to eighteen carbon atoms, attached to either a nitrogen or carbon atom of betaine. As examples may be mentioned octyl, nonyl, decyl, dodecyl, tetradecyl, hexadecyl, octadecyl and 9, 10-octadecenyl betaines of the C- and N-types. Other useful specific compounds are listed in Downing and Johnson application Serial No. 13,664 filed March 29, 1935.

In order that our invention will be more clearly understood a brief description of the same in one embodiment, namely the washing of discharge prints, will be given. White discharge prints on dyeings of direct, after-treated or developed azo

dyes on cotton and rayon are prepared as follows:

The dyed fabric is printed with a British gum paste containing sodium sulfoxylate formaldehyde. The printed fabric is aged in an atmosphere of steam at a temperature above 100° C. The steam decomposes the sodium sulfoxylate formaldehyde with liberation of the sodium sulfoxylate (Na_2SO_2) which in turn reduces the color into amino- and hydroxyaromatic derivatives. These decomposition products, together with the components of the discharge paste are removed by rinsing the discharge print in a bath containing a higher aliphatic sulfate having eight to twenty-four carbon atoms in the form of a water-soluble salt, together with a water-soluble alkaline earth metal salt. This is best accomplished with an alkali metal mono-alkyl sulfate of a chain length of ten to fourteen carbon atoms or an alkali metal unsaturated aliphatic alcohol sulfate of a chain length of sixteen to eighteen carbon atoms. The preferred metal ions are magnesium or calcium. The higher aliphatic sulfate acts as a detergent or a washing agent to remove the portions of the discharge, while the metal ions prevent the removal of dye from the fabric and prevent bleeding into the discharge portions of the same. It is obvious that any water-soluble alkaline earth metal salt may be used in this process provided it acts to repress the bleeding of the dye from the fabric without exerting a deleterious effect on the dyeing or destroying the detergent properties of the fatty alcohol sulfate. Superior results are obtained with calcium chloride and magnesium sulfate.

Excellent results from the washing process are obtained in solutions containing from 0.25 to 5.0 grams per liter of the higher aliphatic sulfate water soluble salts and higher hydrocarbon substituted betaines and either 0.25 to 10.0 g./l. and preferably 1.0 to 5 g./l. of calcium chloride or 0.5 to 20 g./l. and preferably 2 to 10 g./l. of magnesium sulfate (as epsom salt). Concentrations of 1 gram per liter of calcium chloride and 2 to 2.5 grams of magnesium sulfate greatly and even almost completely repress bleeding of the dye from the goods. The ratio of magnesium sulfate (as epsom salt) to the fatty alcohol sulfate may vary from 0.1:1 to 40:1 while the ratio of calcium chloride to fatty alcohol sulfate may vary from 0.05:1 to 40:1 provided the metal ion concentration is within the limits described above. The ingredients may be added to the bath either separately or together, in solid form or in solution.

The processing temperature may vary from 80° F. to 180° F. while the ratio of the volume of the bath to goods may vary from 10:1 to 60:1. The washing period should be for at least one minute but may be extended to fifteen minutes or longer, if desired. The conditions described above are the preferred limits but may be altered to meet any specific requirements which may be encountered.

This invention is not restricted to the use of the fatty alcohol sulfates as detergents. Any detergent having strong scouring properties which is compatible with water-soluble alkaline earth metal salts may be used according to our invention; thus, the higher aliphatic betaine derivatives such as those described in Downing and Johnson application Serial No. 13,664 filed March 29, 1935, give excellent results similar to the higher aliphatic sulfates. Good results are obtained if the alkali metal salts of sulfonated oils, the condensation product of albumin with a

fatty acid, and higher aliphatic amidosulfonates such as $C_{17}H_{35}CONHCH_2CH_2SO_3Na$ are used to replace the higher aliphatic sulfates in the above described processes. These products are all characterized as agents possessing wetting and detergent properties in solution in the presence of calcium and magnesium salts. The higher aliphatic sulfates and aliphatic betaine derivatives are further characterized as having good scouring properties.

Colored discharge prints may be prepared as above with the additional incorporation of a vat color in the discharge paste. The vat color is reduced by the sodium sulfoxylate in the steam ager, simultaneously with the color on the fabric and replaces the discharged ground color by a dyeing process. The colored discharge print is oxidized in an acid solution (e. g. acetic acid) of sodium perborate or sodium bichromate and is washed at a temperature greater than 140° F. to develop the strength and brightness of the vat dye. The other details are as cited in the preceding paragraphs.

The invention will be illustrated but is not limited by the following examples in which the parts are by weight unless otherwise indicated.

EXAMPLE I

A 5% dyeing of "Pontamine" Navy Blue BF (of Color Index 568 type) was prepared on viscose rayon piece goods. A discharge pattern of the dyeing was printed with an engraved roll laboratory machine using a discharge paste containing 20% of sodium sulfoxylate formaldehyde, 75% of gum tragacanth and 5% of glycerin. The discharge print was aged for five minutes at 105° C. in an atmosphere of steam in a Mather and Platt rapid ager. The discharge print was cut into smaller pieces of 3.5 grams each which were washed in various solutions, which are identified in Table I, for three minutes.

dip in cold water, run through squeeze rolls to remove the excess water, and dried with a hot iron. A visual examination of the pieces showed that the strength of the ground color on prints processed in the fatty alcohol sulfate-magnesium or calcium salt baths was appreciably greater (20% or more) than the strength of the ground color on prints rinsed in a fatty alcohol sulfate solution, in a soap solution or in water alone. The differences were more noticeable for prints processed at 160° F. than at 140° F. An examination of the detergent baths following the washing of the prints also showed that much more color was removed from the goods in baths which did not contain the added calcium or magnesium salts in combination with a fatty alcohol sulfate product. This difference in the amount of color removed from the fabric into the bath has a decided bearing on the appearance of the white discharge. The fatty alcohol sulfate-calcium and magnesium salt solutions operated satisfactorily to remove the decomposition products of the discharge together with the discharge paste. There was only a trace staining of the discharged part by bleeding dye even after four prints were washed in the bath. On the other hand, objectionable heavy bleeding of dye occurred into the discharge of prints processed in a fatty alcohol sulfate solution, a soap solution, or in water alone. This objectionable bleeding occurred with the first print rinsed in the bath. It is apparent, on the basis of the observations given above, that a rinse of the discharge print in a fatty alcohol sulfate-calcium or magnesium salt bath is highly advantageous since the ground strength is appreciably stronger and the discharge is much cleaner.

In test baths 24 to 43 the volume of the baths was 200 cc.; three successive prints were washed in each solution. An examination of the prints showed that considerable dye was removed by all detergent solutions in the absence of added elec-

TABLE I

Conditions used for washing prints of "Pontamine" Navy Blue BF on viscose rayon

Bath Number	Detergent concentration, g./l.	MgSO ₄ ·7H ₂ O, g./l.	CaCl ₂ , g./l.	Na ₂ SO ₄ , g./l.	K ₂ SO ₄ , g./l.	Temp., °F.
1	Lorol sodium sulfate, 0.5			0.5		140
2	do.			0.5		160
3-4	do.	7.8	3.5			140
5-6	Lorol sodium sulfate, 2.5	7.8	3.5			140
7	Lorol sodium sulfate, 0.25	2.0				160
8-11	Lorol sodium sulfate, 0.5	4.0				160
12	Lorol sodium sulfate, 1.0	7.8	3.5			160
13-14	Lorol sodium sulfate, 2.5	7.8	3.5			160
15	Ocenol sodium sulfate, 0.5			0.5		140
16	do.			0.5		160
17-18	do.	7.8	3.5			160
19-20	Ocenol sodium sulfate, 2.5	7.8	3.5			160
21	Olive oil soap, 2.5	No electrolyte.				160
22	Olive oil soap, 5.0					160
23	Water					160
24	Lorol sodium sulfate, 2.5			2.5		160
25-26	do.			2.25	2.75	160
27-30	do.	7.8	3.5	11.25	13.75	160
31	Ocenol sodium sulfate, 2.5			2.5		160
32-35	do.	7.8	3.5	2.25	2.75	160
36-37	do.			11.25	13.75	160
38	Olive oil soap, 2.5			2.25	2.75	160
39-40	do.			11.25	13.75	160
41-42	do.			2.25	2.75	160
43-46	Water	7.8	3.5	11.25	13.75	160
47-48	do.					160

In test baths 1 to 23, five pieces of the discharged dyeing on rayon were rinsed successively in a 200 cc. bath under the conditions specified in Table I. The pieces were stirred continuously with a glass rod during immersion. The prints were rinsed free of the detergent solution by a

trolytes and, as a result, the white discharge pattern was colored by the bleeding of the dye. This effect became highly pronounced as successive prints were washed in the bath. The addition of any of the inorganic electrolytes served to reduce the removal of dye from the prints to a degree

that varied with the electrolyte used and its concentration in the bath. At equivalent ion concentrations, the calcium and magnesium salts were more effective than the sodium and potassium salts in preventing removal of dye. The calcium chloride at 3.5 g./l. and the magnesium sulfate at 7.8 g./l. were more effective than sodium sulfate at 11.25 g./l. or potassium sulfate at 13.75 g./l. At these concentrations the sodium and potassium ions are present at five times the ion concentrations of magnesium and calcium ions in the solutions.

While the potassium and sodium salts decreased the removal of the color from the goods, they also functioned in these experiments to cause redyeing of the discharged portions by the bleeding color. As a result, prints washed in the detergent solutions containing sodium sulfate at 2.25 g./l. and potassium sulfate at 2.75 g./l. were much more intensely colored in the discharged portion than those washed in solutions of the detergent alone. The effect was highly pronounced as successive prints were washed in the same bath. At concentrations of 11.25 g./l. of sodium sulfate and 13.75 g./l. of potassium sulfate the initial prints washed in the detergent solutions were much more highly colored than when processed with the detergent alone. As successive prints were processed in solutions containing these high salt concentrations the discharged portions were highly colored but not to the degree noted in washing in a solution of the detergent alone.

The calcium and magnesium salts added to solutions of the long chain fatty alcohol sulfate products not only prevented heavy bleeding of the color from the prints, but also served to prevent redyeing of the white discharge pattern by any color that was removed. As a result, the discharge remained uncolored by more than a trace of the dye as successive prints were washed in the bath and the prints obtained were superior as progressive tests were made in the baths to any prints processed by the detergents alone or with the detergents combined with sodium and potassium salts.

Prints washed in solutions of the electrolytes alone without a detergent were not properly cleansed in the discharge portion. The discharges were appreciably yellow in appearance. While

that in washing discharge prints it is not sufficient that an added electrolyte to the detergent bath repress the bleeding of dye from the goods. It is in addition necessary that the inorganic salt act on any removed dye so that it will not be readsorbed on the pattern. It is pointed out that the calcium and magnesium salts are not only more effective than are sodium and potassium salts in preventing the removal of color from dyeings by the detergents with which they are compatible, but that the calcium and magnesium salts also prevent more than a trace of redyeing of pattern effects on the goods by any dye which is removed. The experimental evidence shows that the presence of sodium and potassium salts in the bath at reasonable concentrations does not prevent appreciable readsorption of dye on the discharge pattern.

The term "Lorol" describes the fraction of saturated alcohols, obtained by hydrogenation of coconut oil, which is composed mainly of C₁₂ and C₁₄ alcohols together with smaller amounts of C₁₆ and C₁₈ alcohols.

The term "Ocenol" covers a mixture of saturated and unsaturated long chain fatty alcohols, mainly of chain length C₁₆ and C₁₈ and of an iodine number of approximately 60.

Similar results were obtained with the following colors: 8% "Pontamine" Fast Black PG Extra of the type set forth in U. S. Patent 536,431, "Pontamine" Fast Red 8BL, 6% (Color Index #278), "Pontamine" Fast Red F, 6% (Color Index #419), "Pontamine" Bordeaux B, 4% (Color Index #375), "Pontamine" Blue RW, 4% (Color Index #512), "Pontamine" Fast Yellow 4GL, and 4% (Color Index #349).

The general processes as outlined above were used advantageously for washing white discharge prints of direct or substantive colors on cotton. For example:

EXAMPLE II

A 2% dyeing of the direct color Du Pont Purpurine 4B (Color Index #448) on cotton broadcloth was discharged as in Example I, and cut into small pieces. Comparative tests were made of the efficiency of different detergent compositions, by rinsing 5 gram discharge prints at 80° F. in different detergent baths of composition as given in Table II, for two minutes.

TABLE II
Conditions for washing discharge prints of direct dyes on cotton

Bath Number	Detergent concentration g./l.	MgSO ₄ ·7H ₂ O, g./l.	CaCl ₂ , g./l.	Na ₂ SO ₄ , g./l.	Temp., °F.
1	Lorol sodium sulfate, 0.25	-----	-----	0.25	80
2	Lorol sodium sulfate, 1.25	-----	-----	1.25	80
3-6	Lorol sodium sulfate, 0.125	3.1 15.5	1.4 7.0	-----	80
7-13	Lorol sodium sulfate, 0.25	2.5, 3.1, 10, 15.5, 25.	1.4 3.5	-----	80
14-16 17-19	Lorol sodium sulfate, 0.5	2.5, 10, 25	-----	-----	80
20-22 23-24	Lorol sodium sulfate, 1.25	2.5, 3.1, 10, 15.5, 25.	1.4 3.5 7.0	-----	80
25	Decyl sodium sulfate, 0.08	-----	-----	0.08	80
26	Decyl sodium sulfate, 0.44	-----	-----	0.44	80
27-28	Decyl sodium sulfate, 0.08	-----	1.4 3.5	-----	80
29-30	Decyl sodium sulfate, 0.44	-----	1.4 3.5	-----	80
31	Water	No electrolyte	-----	-----	80

the inorganic salts prevented the substantial removal of dye from the prints, they did not exercise any detergent action.

These latter tests, as well as tests 1 to 23 show

These tests were run in 200 cc. of the detergent. The pieces were stirred continuously during the immersion period and then were removed and rinsed with water at 110°-120° F. to remove the

detergent from the fabric. The pieces were run between squeeze rolls to expel the excess water and were dried with a hot iron. It was shown, as a result of the tests, that a rinse in a bath

Example I. Five gram pieces of the prints were washed at 120° F. in baths identified in Table III containing magnesium sulfate and calcium chloride.

TABLE III

Conditions for washing discharge prints of direct dyes on cotton

Bath number	Detergent concentration, g./l.	MgSO ₄ ·7H ₂ O, g./l.	CaCl ₂ , g./l.	Temp., °F.	Time, minutes
1-2	Praestab oil, 2.5	7.8	3.5	120	2
3-4	Avirol AH extra, 2.5	7.8	3.5	120	2
5-6	Albumen fatty acid condensation product, 2.5	7.8	3.5	120	2
7-8	C ₁₇ H ₃₅ CON(CH ₃)—CH ₂ CH ₂ SO ₃ Na, 2.5	7.8	3.5	120	2
9-10	N-stenyl betaine, 0.75	7.8	3.5	160	3
11	Olive oil soap, 2.5			120	2

containing a fatty alcohol sulfate in combination with a calcium or a magnesium salt produces noticeably better white discharges than does water or solutions of the fatty alcohol sulfate alone. The bleeding of dye from the fabric in a fatty alcohol sulfate-magnesium or calcium salt bath is less than in water or in solutions of the fatty alcohol sulfate alone. As a result, the strength of the ground color of prints processed in a fatty alcohol sulfate-calcium or magnesium salt solution is greater than the strength obtained following processing by the other methods while the appearance of the white discharges is noticeably better.

Tests similar to those outlined above were made with discharge prints of "Pontamine" Fast Scarlet 4BS, 2% (Color Index #326, listed as a specific type of color but chemical identity is not revealed), "Pontamine" Black E, 6% (Color Index #581), and "Pontamine" Green S Conc., 2% (Color Index #583). The results obtained in the tests again showed that advantages similar to those cited above are obtained when the discharge prints are processed in a bath containing a fatty alcohol sulfate in combination with a calcium or a magnesium salt.

At temperatures of 120° F., similar results were obtained with "Du Pont" Purpurine 4B (Color Index #448), "Pontamine" Fast Red 8BL, 2% (Color Index #278), "Pontamine" Fast Scarlet 4BS, 2% (Color Index #326), "Pontamine" Fast Orange S, 2% (Color Index #326, not identified as a chemical individual), "Pontamine" Black E (Color Index #581), "Pontamine" Fast Scarlet 4BS, 2% (Color Index #326, chemical identity not given), "Pontamine" Fast Orange S, 2% (Color Index #326, chemical identity not given), "Pontamine" Yellow CG, 2% (Color Index #411), "Pontamine" Fast Yellow 4GL, 2% (Color Index #349), "Pontamine" Fast Orange WS, 2% (Color Index #326, chemical identity not given), "Pontamine" Brown CG, 2% (Color Index #598), "Pontamine" Blue 3R, 2% (Color Index #464), "Pontamine" Green GX, 2% (Color Index #594), "Pontamine" Black E, 2% (Color Index #581) and "Pontamine" Green S Conc., 2% (Color Index #583).

EXAMPLE III

A 2% dyeing of "Pontamine" Blue RW (Color Index #512) on cotton was discharged as in

In these tests the white discharge pattern was cleansed to a greater degree using a detergent agent in the presence of the metal ions than by water alone. When detergent agents were present all of the prints were satisfactorily cleaned to produce a good white discharge pattern. Practically no bleeding of the dye occurred into the baths. The discharge patterns processed as above with soap solutions were highly discolored by the bleeding of the dye into the discharged portion. The discharge pattern obtained from the water rinse was dull and tinted by bleeding dye. The prints washed with solutions containing the higher hydrocarbon substituted betaines in addition to having the advantages listed above were very soft to the feel.

Results similar to those described above were obtained with "Pontamine" Black E (Color Index #581), "Pontamine" Green S Conc. (Color Index #583), "Pontamine" Fast Orange WS (Color Index #326, listed as class), "Pontamine" Fast Blue 3R (Color Index #464), "Pontamine" Fast Orange S (Color Index #326, chemical identity not given), "Pontamine" Fast Red 8BL (Color Index #278), "Pontamine" Brown CG (Color Index #598), and "Pontamine" Green GX (Color Index #594).

There are a number of direct dyes whose wash fastness is improved by after-treatments, as for example treating in a bath containing formaldehyde and acetic acid. This after-treatment is often utilized in discharge work to improve the fastness of the ground color so that a more vigorous soaping of the discharge print may be used to remove the products of the discharge and the discharge paste. The process for washing prints as outlined above, utilizing fatty alcohol sulfates in combination with calcium and magnesium salts as a detergent medium, has been used advantageously in washing discharge prints on after-treated dyeings. For example:

EXAMPLE IV

A 5% dyeing of "Pontamine" Navy Blue BF (of Color Index 568 type) on rayon was after-treated with formaldehyde and acetic acid. A discharge print was prepared as in Example I. Comparative tests were made in which 3.6 gram pieces of the print were rinsed in detergent baths of the composition outline in Table IV, for a period of three minutes.

TABLE IV
Conditions for washing discharge prints of after-treated dyes on rayon

Bath number	Detergent concentration, g./l.	MgSO ₄ ·7H ₂ O, g./l.	MgCl ₂ ·6H ₂ O, g./l.	CaCl ₂ , g./l.	Temp., °F.
1-2	Lorol sodium sulfate, 0.5	7.8		3.5	140
3-4	Lorol sodium sulfate, 2.5	7.8		3.5	140
5-7	Lorol sodium sulfate, 0.5	7.8	6.45	3.5	160
8-10	Lorol sodium sulfate, 2.5	7.8	6.45	3.5	160
11-12	Ocenol sodium sulfate, 0.5	7.8		3.5	160
13-14	Ocenol sodium sulfate, 2.5	7.8		3.5	160
15	Sodium oleate, 5.0	No electrolyte			140
16	do.	do.			160

In these tests, five pieces of the discharged dyeing were rinsed successively in a 200 cc. bath under the conditions specified in Table III. The prints were rinsed free of the detergent solution by several dips in cold water, run through squeeze rolls to remove the excess water, and dried with a hot iron. A visual examination of the prints showed that the results obtained were quite similar to those obtained by similar rinses of the unafter-treated dyeing as described in Example I. The strength of the ground color on prints rinsed in a fatty alcohol sulfate-magnesium or calcium salt bath was appreciably (more than 20%) greater than the strength of the ground color on prints rinsed in the soap solution. The differences obtained were greater at 160° F. than at 140° F. An examination of the detergent baths following the washing operation showed that much more color was removed by the soap than by the other detergent solutions. The excessive bleeding of the dye into the soap solution was reflected in a heavy staining of the discharge. The stain became even heavier as successive prints were washed in the bath. On the other hand, there was only a trace staining of the discharge of prints rinsed in a fatty alcohol sulfate-magnesium or calcium salt solution. A comparison of the discharge prints of the after-treated dyeings in this example with discharge prints of the unafter-treated dyeings of the same color under Example I show that of corresponding prints, the appearance of the after-treated was better than the appearance of the unafter-treated samples. However, the results obtained for prints of the unafter-treated dyeing rinsed in a fatty alcohol sulfate-magnesium or calcium salt bath

have found limited use in practice not only because of the difficulty in preparing satisfactory discharge patterns on these colors but also because of their poor fastness to soaping in the customary laundry practice. As a result, the developed class of dyes, which possess much better fastness to soaping, has been much more widely used for ground colors in discharge printing. In applying this type of color, a dyeing of a direct dye, containing a diazotizable amino group, is diazotized with nitrous acid and is coupled with an aromatic or heterocyclic component containing no acid groups. Examples of widely used developers are beta-naphthol, m-toluylene diamine, and phenyl methyl pyrazolone. The developed class of dyestuffs does not possess absolute wash fastness, i. e. an appreciable bleeding of most dyes occurs into a soap solution. As a result the difficulties in processing prints of the direct and after-treated class of dyes are found to occur to a smaller degree with the developed colors. Tests were made in which discharge prints of the developed types of dyes were rinsed advantageously in a bath containing a fatty alcohol sulfate or a higher aliphatic hydrocarbon substituted betaine in combination with a calcium or a magnesium salt. For example:

EXAMPLE V

A discharge pattern was printed as under Example I on a 3% dyeing of "Pontamine" Diazo Blue BR (Color Index #317) (Developer beta-naphthol) on rayon. Comparative tests were made by rinsing 3.5 gram pieces of the discharge print in detergent baths of the composition given in Table V.

TABLE V
Conditions for washing discharge prints of developed dyes on rayon

Bath number	Detergent concentration, g./l.	MgSO ₄ ·7H ₂ O, g./l.	CaCl ₂ , g./l.	Temp., °F.	Time, minutes
1	Lorol sodium sulfate, 0.5			160	3
2	Lorol sodium sulfate, 2.5			160	3
3-5	Lorol sodium sulfate, 0.5	1.6, 4.0, 8.0	3.5	160	3
6-7			14.0		
8-10			3.5	160	3
11-12	Lorol sodium sulfate, 2.5	1.6, 4.0, 8.0	14.0		
13-14	Ocenol sodium sulfate, 0.5, 2.5			160	3
15-17	Ocenol sodium sulfate, 0.5	1.6, 4.0, 8.0	3.5	160	3
18-19			14.0		
20-22			3.5	160	3
23-24	Ocenol sodium sulfate, 2.5	1.6, 4.0, 8.0	14.0		
25-26	N-stenyl betaine, 0.15	7.8	3.5	160	3
27-28	N-stenyl, betaine, 0.75	7.8	3.5	160	3
29	Sodium oleate, 5.0	No electrolyte		160	3

were vastly superior to the results obtained by treatment of an after-treated dyeing in a soap solution.

The direct dyes as well as dyes which are after-treated with formaldehyde and acetic acid

In these tests four successive pieces of the discharge print were processed in detergent baths of 200 cc. volume. The pieces were further rinsed in water at about 110° F. for thirty seconds to remove the detergent solution and then

dried with a hot iron. A visual examination of the pieces showed that the white discharge obtained from the initial piece was not greatly different by the various methods of rinsing given in Table V. However, much more bleeding of dye from the print occurred into the soap solution and into the solutions containing the fatty alcohol sulfates alone. As a result, the white discharges of successive prints processed in these baths became highly stained with dye. On the contrary, very little bleeding of the dye occurred in the fatty alcohol sulfate or higher hydrocarbon substituted betaine salt detergent baths and, as a result, successive prints rinsed in these baths remained uniform in quality. The differences encountered in the amount of bleeding into the detergent baths were reflected in the strengths of the ground color on the prints. Prints processed in a soap solution, or in a fatty alcohol sulfate solution alone were 10-20% weaker than prints processed in a fatty alcohol sulfate-magnesium or calcium salt bath.

Tests similar to those outlined above were also carried out with "Pontamine" Diazo Black BHSW, 6% (developer meta-toluylene diamine) (Color Index #401). The results obtained in comparative tests with these colors showed an improvement in the fatty alcohol sulfate-magnesium and calcium salt solutions which varied with different dyes but which were essentially similar to that described above. Similar results were obtained with the higher betaines listed. The prints being very soft to the touch.

A "steryl" radical is similar in nature to the lorol radical, being a mixture of higher hydrocarbon radicals containing essentially sixteen and eighteen carbon atoms but also containing some twelve, fourteen and twenty carbon atoms.

EXAMPLE VI

A product containing about 7% of N-octadecyl betaine and about 5% of N-hexadecyl betaine together with smaller amounts of N-dodecyl betaine and N-myristyl betaine and about 84% of $MgSO_4 \cdot 7H_2O$ was prepared by mixing the ingredients in a mortar and pressing into the form of a cake with a hydraulic press under 1000 lbs./sq. in. pressure. About 0.5 gram of the product was dissolved in 200 cc. of water at 160° F. and the solutions used to rinse white discharge prints of "Pontamine" Diazo Blue BR. (Color Index #317) as in Example V. The use of the product just described gives results markedly superior to soap for rinsing the discharge prints since practically no bleeding of the dye occurs to decrease the ground strength or to color the white discharge. Similar cakes may be prepared from the individual or mixed higher aliphatic sulfates and higher betaines of the C and N types described early in this case.

A fatty alcohol sulfate together with a magnesium or a calcium salt was used advantageously in processing colored discharge prints on rayon. For example:

EXAMPLE VII

A discharge print of "Leucosol" Blue G (Color Index 1113) was printed on a 6% dyeing of "Pontamine" Fast Red F (Color Index #419) by the following procedure: The dyeing was printed by means of an engraved roll laboratory machine with a discharge paste containing 20% "Leucosol" Blue G, 12.8% sodium sulfoxylate formaldehyde,

15.2% potassium carbonate, 44% British gum tragacanth, 4% glycerin, and 4% water. The print was aged for five minutes at 105° C. in an atmosphere of steam in a Mather-Platt rapid ager and was then oxidized for two minutes room temperature in a solution containing 0.5% of sodium perborate and 0.5% acetic acid at room temperature. Comparative tests were made of methods for washing the prints by rinsing 3.5 gram pieces in detergent baths of the composition given in Table VI.

TABLE VI

Conditions for rinsing colored discharge prints on rayon

Bath number	Detergent concentration, g./l.	MgCl ₂ ·6H ₂ O g./l.	Temp., °F.	Time, minutes
1.....	Lorol sodium sulfate, 0.5.	6.45	160	5
2.....	Lorol sodium sulfate, 2.5.	6.45	160	5
3.....	Olive oil soap, 5.0.....	-----	160	5

In these tests, three successive prints were washed in baths of 200 cc. volume. The pieces were then rinsed at 100° F. in water to remove the detergent solution and were dried with a hot iron. A visual examination of the pieces showed that the blue discharge portions of prints rinsed in the lorol sodium sulfate-magnesium chloride solutions were appreciably brighter than when rinsed in a soap solution. Very much less bleeding of the ground color occurred in the fatty alcohol sulfate-magnesium chloride solutions than in the soap solution. The improvement in the brightness of the "Leucosol" Blue G discharges obtained by rinsing in the sodium lorol sulfate-magnesium chloride solutions was probably due to the fact that there was much less bleeding of the ground color in these baths. It was also observed that the strength of the ground color was appreciably greater on dyeings which were processed in the fatty alcohol sulfate-magnesium chloride solutions.

Tests similar to those given above were carried out with discharge prints of "Leucosol" Blue G on dyeings of "Pontamine" Fast Red 8BL, 6% (Color Index #278), "Pontamine" Bordeaux B, 4% (Color Index #375), "Pontamine" Blue RW, 4% (Color Index #512), and "Pontamine" Fast Yellow 4GL (Color Index #349) all on rayon. An improvement was observed in the appearance of the discharge prints processed in a fatty alcohol sulfate-magnesium chloride solution which was similar to that described above.

EXAMPLE VIII

A 5% dyeing of "Pontamine" Navy Blue BF (of Color Index 568 type) was after-treated with formaldehyde and acetic acid at 120° F. and was printed by means of an engraved roll laboratory machine with a discharge paste containing 15% "Sulfanthrene" Scarlet GC a dye of the thioindigo type, 40% British gum and the other components as described in Example VII. The print was agent and oxidized as described in Example VII. Comparative tests were made of the efficiency of various detergent baths of the composition described in Table VII.

TABLE VII

Conditions for rinsing colored discharge prints on rayon

Bath number	Detergent concentration, g./l.	MgSO ₄ ·7H ₂ O, g./l.	CaCl ₂ , g./l.	Temp., °F.	Time, minutes
1-2	Lorol sodium sulfate, 0.5, 2.5			160	3
3-4	Lorol sodium sulfate, 0.5	7.8	3.5	160	3
5-6	Lorol sodium sulfate, 2.5	7.8	3.5	160	3
7-8	Ocenol sodium sulfate, 0.5, 2.5			160	3
9-10	Ocenol sodium sulfate, 0.5	7.8	3.5	160	3
11-12	Ocenol sodium sulfate, 2.5	7.8	3.5	160	3
13	Olive oil soap, 5.0			140	3
14	do			160	3

In these tests 3.5 gram pieces of the discharge print were rinsed in 200 cc. of the detergent solution for three minutes, then removed and freed of the detergent by a half minute rinse in water at 110° F. The excess water was removed by squeeze rolls and the print was dried with a hot iron. A visual examination of the prints showed that the strength of the ground color of all prints washed in a fatty alcohol sulfate-magnesium or calcium salt bath was appreciably greater (10-20%) than that obtained by processing in a soap solution or in a solution of a fatty alcohol sulfate alone. The colored discharge portion of the print was of about the same strength and brightness, regardless of the method employed.

EXAMPLE IX

A 6% dyeing of "Pontamine" Diazo Black BHSW (developer meta-toluyene diamine) (Color Index #401) was printed, by means of an engraved roll laboratory machine, with a discharge paste containing 15% "Sulfanthrene" Scarlet G of the thioindigo type 49% British gum, 12.8% sodium sulfoxylate formaldehyde, 15.2% potassium carbonate, 4% glycerin and 4% water. The print was aged and oxidized as described under Example VII. Tests of the efficiency of different detergent compositions were carried out as described under Example VIII. The results obtained showed that the rinsing of prints in baths containing fatty alcohol sulfates together with calcium or magnesium salts give the same advantages as are described under Example VIII.

The above examples, it will be noted, are directed to the washing of discharge prints on cotton and rayon and to the making of detergent solutions and detergent compositions in cake form. Our invention is not to be limited to the washing of such white or colored discharge prints, although that represents the preferred embodiment thereof. Discharge printings on silk and wool may be washed in a similar manner with excellent results.

The process is obviously not limited to the washing of discharge prints but may be used in washing any colored textile material, especially those with which a detergent action is desired and during which it is desirable to prevent bleeding of the dye from the fabric. The fabrics which may be processed include not only cotton and rayon, but also wool and silk (weighted and unweighted) and fabrics composed of artificial fibers of the cellulose ether and ester type such as cellulose acetate, and any fabrics which may be formed by combinations of these materials. The dyes subject to treatment are not limited to the specific examples and types of colors covered but may be of any that are temporarily or perma-

nently fixed on the fabric by the presence of the metallic ion or ions in the bath. The concentrations of the detergents, the temperatures, and the length of time for processing cover the preferred limits for the invention but do not preclude the use of concentrations outside the limits which may prove better adapted to gain a desired result.

The following examples illustrate the utility of our process in washing dyed fabrics other than discharge prints with the detergent compositions of the present invention.

EXAMPLE X

- Dyeings on cotton fabrics of
- (1) Meta toluidine-bis-azo - 1 - naphthylamine-4-sulfonic acid (sodium salt)
 - (2) (Color Index #478) ortho toluidine-bis-azo-1-naphthylamine-4-sulfonic acid (sodium salt)
 - (3) (Color Index #278) p-sulfobenzene-azo-benzene-azo-6-benzoyl-amino-1-naphthol-3-sulfonic acid (sodium salt) and
 - (4) p-Sulfobenzene-azo-benzene-azo-6-benzoyl-p-aminobenzoyl-amino-1-naphthol-3-sulfonic acid (sodium salt)

were rinsed for one hour at 50° C. (120° F.) in 250 cc. of a 1.0 g./l. solution containing a mixture of octyl and decyl sodium sulfates in the proportion of 8 to 3. Corresponding tests were also made in solutions containing varying amounts of calcium chloride and magnesium sulfate in addition to the sodium alkyl sulfate. The results giving the per cent of dye removed by detergent solutions of varying composition are contained in Table VIII.

TABLE VIII

Per cent of dye removed by the above alkyl sulfate in admixture with metal salts

Dye	Alone	+MgSO ₄			+CaCl ₂	
		.005N	.01N	.025N	.005N	.01N
1	54.3	18.7	17.2	26.9		
2	29.9	0.9	1.0	1.4		
3	71.6	41.8	30.2	22.6	34.7	23.2
4	24.3	2.6	1.1	1.4	0.9	0.4

It is shown by these results that calcium and magnesium salts act to repress markedly the bleeding of these dyes into the detergent solution.

This invention presents the advantage that a detergent cake of general utility in preparing washing solutions which will prevent the bleeding of a dye may be easily prepared. The invention presents the additional advantage that clean discharge prints which are of good strength and color can be quickly and economically obtained. An additional advantage resides in the

fact that a washing solution can be used for washing a large volume of goods before it needs replacement by a fresh solution. Another advantage resides in the fact that redyeing of the fabric does not occur in our detergent baths. Another important advantage resides in the fact that discharge prints and dyed fabrics which are soft to the touch are obtained especially with the higher aliphatic hydrocarbon substituted betaines. Other advantages will be obvious to those skilled in the textile and related arts.

As many widely different embodiments of the invention may be made without departing from its spirit and scope, it is to be understood that the invention is not limited to the specific embodiments hereinbefore set forth, except as defined in the appended claims.

We claim:

1. The process which comprises coloring a fabric with a water-soluble azo dye, discharging selected portions of the dye and washing the fabric with an aqueous solution containing a water-soluble alkaline earth metal salt and a detergent compatible therewith which has strong scouring properties taken from the class consisting of long chain aliphatic hydrocarbon sulfates and higher hydrocarbon substituted betaine derivatives.

2. The process which comprises coloring a textile fabric from the class consisting of cotton and viscose rayon with a water-soluble azo dye, discharging selected portions of the dye with a reducing composition containing a reducing agent, and washing the fabric with an aqueous solution containing a water-soluble alkaline earth metal salt and a water soluble salt of an aliphatic hydrocarbon sulfate having from eight to eighteen carbon atoms.

3. The process which comprises coloring a textile fabric from the class consisting of cotton and viscose rayon with a water-soluble azo dye, discharging selected portions of the dye with a reducing composition containing a reducing agent, and washing the fabric with an aqueous solution containing a water-soluble alkaline earth metal salt and an alkali metal salt of an aliphatic hydrocarbon sulfate having from eight to eighteen carbon atoms.

4. The process which comprises coloring a textile fabric with a water-soluble dye, discharging selected portions of the dye with a reducing composition containing a vat dye, oxidizing the vat dye and washing the fabric with an aqueous solution containing a water-soluble alkaline earth metal salt and a detergent compatible therewith which has strong scouring properties taken from the class consisting of higher aliphatic hydrocarbon sulfates and higher hydrocarbon substituted betaine derivatives.

5. The process which comprises coloring a textile fabric from the class consisting of cotton and viscose rayon with a water-soluble azo dye, discharging selected portions of the dye with a reducing composition containing sodium sulfoxylate formaldehyde and a vat dye, oxidizing the vat dye, and washing the fabric with an aqueous solution containing a water-soluble alkaline earth metal salt and an alkali metal aliphatic hydrocarbon sulfate having a chain of eight to eighteen carbon atoms.

6. The process which comprises coloring a textile fabric from the class consisting of cotton and viscose rayon with a water-soluble azo dye, discharging selected portions of the dye with a reducing composition containing sodium sulfoxylate formaldehyde and a vat dye, oxidizing the vat dye, and washing the fabric with an aqueous solution containing a water-soluble alkaline earth metal salt and a higher hydrocarbon substituted betaine.

7. The process which comprises washing dyed fabrics dyed with a water-soluble dye with an aqueous solution containing an alkaline earth metal salt and a detergent compatible therewith which has strong scouring properties taken from the class consisting of long chain aliphatic hydrocarbon sulfates and higher hydrocarbon substituted betaine derivatives.

8. The process which comprises washing discharge prints dyed with a water-soluble dye with an aqueous solution containing a water-soluble alkaline earth metal salt and an aliphatic sulfate having eight to eighteen carbon atoms.

9. The process which comprises washing discharge textile prints dyed with a water-soluble azo dye with an aqueous solution containing a water-soluble alkaline earth metal salt and an alkali metal aliphatic sulfate containing a carbon chain of eight to eighteen carbon atoms.

10. A process as set forth in claim 9 wherein the salt is magnesium sulfate.

11. A process as set forth in claim 9 wherein the salt is calcium chloride.

12. The process which comprises washing discharge textile prints dyed with a water-soluble azo dye with an aqueous solution containing an alkaline earth metal salt from the class consisting of calcium and magnesium and a detergent having strong scouring properties taken from the class consisting of long chain aliphatic sulfates and long chain aliphatic betaine derivatives.

13. A process as set forth in claim 12, wherein the salt is magnesium sulfate.

14. A process as set forth in claim 12 wherein the salt is calcium chloride.

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