The direct dyeing of the vegetable as well as of the animal fibre with water-soluble dyestuffs is the simplest of all dyeing methods and at the same time the most harmless one for the fibre.

There is, however, the disadvantage of a more or less remarkable lack of fastness of the dyed materials to water and washing. Though there are in the present art a great number of processes to overcome this deficiency, these processes take, however, a certain constitution of the dyestuff for granted, their performance is in many cases rather complicated and none of them leads to a process such as is attainable by means of the vat-, sulphur- and ice-colours.

Now a process has been found which permits one to render more or less fast to washing any direct-dyeing performed on fibres of natural or regenerated cellulose. This process differs principally from the usual methods of increasing fastness in so far as the effect is not obtained by augmenting the molecule by adding water-insoluble residues to the dyestuff molecule, but by rendering ineffective the groups—especially sulphho- or carboxyl groups—which bring about the water-solubility of the dyestuff and consequently its unfastness. This is obtained by forming salts which are absolutely insoluble and also resistant against the reaction of acids and alkalis as well as against soap. The ammonium amonion bases containing a system of no less than 3 non-interrupted conjugated double bonds, possessing substantial properties, have been recognized as eminently fit for the formation of such insoluble salts. These conjugated double bonds may belong either to open chains or to ring systems which may seem to be interrupted by imino groups in which cases I assume that, for instance, the group —CO—NH acts in the enolic form —C(=O)—N—, so that really no interruption of double linkings occurs. The new process consists therefore in the following: one begins with a direct dyeing on the fibre in the usual manner, WHEREUPON the preliminarily dyed fibre is treated, with or without an intermediate rinsing, in a second bath with the solution of a salt of the quaternary ammonium base which forms an insoluble salt; then one rinses, one soaps once more should it be necessary, one rinses again and finally one dries. If the dye is extracted completely or almost completely from the dyeing bath, it is preferable to go directly to the exhausted dye bath also the ammonium base. It is not necessary that the quaternary ammonium base be colourless, but it may also be of a dyestuff character so that it is able to intensify the dying or to accelerate it off or to alter it completely.

This special feature of the present process offers the advantage that for the obtaining of a predetermined colour intensity one needs only about half of the amount of acid or basic dyestuffs in comparison with the amount required for an ordinary direct dyeing; in consequence of which the dyestuff is extracted from the bath relatively more intensively or even completely so that the aforementioned single-bath-procedure will be applicable.

From the experiments so far made it was discovered that substantive quaternary ammonium bases with at least two quaternary ammonium groups are particularly capable of making organic compounds of an acid character fast to washing on the cellulose fibre.

The aforementioned after-treatment is of a prime importance for the mordant-dyeing direct cotton dyestuffs because the dyed material can thus be mordanted and rendered fast to washing in one and the same bath.

Further it has been stated, that it is also practicable to proceed inversely by treating the fibre first with the solution of the substantive quaternary ammonium base and after that with the dyestuff solution without its making any difference whether the ammonium base is colourless with the result that it serves so to speak merely as a mordant for the dyestuff to be laid upon, or whether it also has colouring properties. Under certain circumstances it is not necessary that the dyestuff itself possess any affinity for the fibre and the former will nevertheless be fixed upon the latter though it will not be fast to washing. From this procedure there results the valuable practical procedure of tinging for instance the vegetable fibre after a preliminary treatment with a substantive, basic mordant of the above characterized sort, with so-called acid wool dyestuffs which are not substantive or only to a little degree, while in many cases they distinguish themselves from the really substantive dyestuffs by cheapness and higher fastness to light.

If the ammonium base be at the same time a dyestuff, it is not necessary that the acid component be likewise a dyestuff and it may therefore be represented by any higher molecular organic compound of an acid character, in which instance it is the chief consideration that the latter forms an insoluble salt with the base. In certain cases it is advantageous if it possesses an affinity for the fibre such as is known for instance of certain sulfonized phenols. Substituted or non-substituted aromatic or sulphonated acids of the phthalic, alicyclic, aromatic or fatty aromatic series are here likewise to be considered.

Besides the dyeing effects it is possible to obtain at the same time a further refining effect consisting in rendering the textile goods supple, of a soft handle and of a water repelling property and with artificial silk one obtains certain matting effects, provided that as acid components one chooses soap forming carbonic or sulphonated fats.
and oils or higher molecular fatty alcohol sulphonates. Merely the latter refining effects are obtained if one combines a colourless, substantive ammonium base with the just named carbonic or sulphonic acids etc., whereby it is of course also practicable to replace part of the components by dyestuffs and thus to accomplish in one and the same operation the dyeing and the further refining.

As acid components one may also employ natural or artificial tanning principles, either alone or together with acid dyestuffs. In this case it is of practical interest to employ natural tanning principles of the pyrogallol- or ellagene tannic acid category. It is already known that these tanning principles, by an after-treatment on the fibre with copper- and chromium salts, produce shades of an excellent fastness to light, while their fastness to washing can now be increased in the desired manner by adding the salt of a suitable substantive quaternary ammonium base in the same way as above described for mordant-drawing dyestuffs. As acid components there are finally to be considered the above mentioned substantive compounds obtainable by sulphurizing of phenols and known for instance under the name of "katanoles". It has already been suggested to render the direct dyeing on the fibre fast to water and wet-ironing and in certain cases even fast to after-dyeing by an after-treatment with amines or ammonium bases containing a high molecular fatty acid residue. This process produces, however, no fastness to washing and merely a quite imperfect improvement.

Example 1

A 2% dyeing of Congo-red performed in the usual manner on cotton, is rinsed and wrung out, then it is treated for half an hour at 90–100° C. in a bath containing 1 g. per liter of the methylsulphuric salt of a substantive disazoammonium base of the following constitution:

\[
\text{CH}_3\text{CH} = \text{CO} = \text{CO} = \text{NH} = \text{NO} = \text{NH}
\]

whereupon it is taken out, rinsed and dried. The thus obtained tone which compared with the original dyeing shows a more yellowish shade, shows an excellent fastness to washing when treated for half an hour in a 0.2% soap solution at 90–100° C., whereas the original dyeing will under the same conditions heavily bleed out into the soap bath and in a great part is drawn off from the fibre.

The above mentioned base is obtained by coupling tetrazotized benzidine with dimethylaniline and addition of dimethylsulphate to the azodyestuff in a nitrobenzol-solution at about 120–150° C. The methylsulphuric salt is yellow, very easily soluble in water and hygroscopic.

Example 2

One makes next in the usual manner a 2% dyeing of direct-darkblue SW (Schultz-Julius, Farbstofftabellen 1914, Nr. 462) on cotton, then 70 one rinses, whereupon the material is brought in wet state and at a temperature at about 40° C. into a bath containing 2% of a substantive basic dyestuff, obtainable by acid coupling of 1 molecule of diazotized trimethyl-m-aminophenylaminom chloride with 1 molecule of a-naphthol

and by combination of the thus formed monazo dyestuff in alkaline solution with 1 molecule of diazotized tolusafranine (Schultz-Julius, I. c. Nr. 679). Then one heats up to 95–100° C. and keeps this temperature for 25 to 30 minutes, whereupon one rinses and dries. As a result a very good black dyeing fast to washing is obtained.

Example 3

Cotton is dyed under usual conditions with 1% of benzo-light-blue FR (cf. Pfe crim-David, Grundlegende Operationen der Farbenchemie, 1922, p. 147) from a neutral bath containing common salt. The dyestuff having completely been drawn on the fibre, one adds immediately and in the form of a hot concentrated solution 1.5% of the reddish blue, substantive dyestuff prepared by diazotizing and coupling of 2 molecules of tolusafranine with 1 molecule of a-naphthol; the bath is kept at boiling temperature until the second dyestuff is likewise drawn on entirely or almost entirely, whereupon one rinses and dries. The thus obtained blackblue dyeing is of an excellent fastness to washing and light.

Example 4

Cotton or viscose-artificial silk is worked for 45 minutes and at 85–100° C. in a bath which in a bath-length of 1:15 contains 2% of an ammonium salt of the following constitution:

\[
\text{CH}_3\text{CH} = \text{CO} = \text{CO} = \text{NH}
\]

whereupon one reduces the nitro group to the amino group and the thus obtained intermediate product is condensed with 2 mols of diazotized trimethyl-m-aminophenylanilid in a bath containing 2% of the substantive basic dyestuff and obtained by the coupling of 2 mols of diazo-

Further 5% of acetic acid and 20% of common salt. Then one washes cold, whereupon the material while moist is brought into a dyeing bath at a temperature of 60° C. containing 1% of Orange II (Schultz-Julius, I. c. Nr. 145) or of another acid wool dyestuff and 20% of common salt in a bath-length of 1:20. The dyeing bath will be exhausted in a short time.

The above substantive ammonium base can be obtained in the following manner: p-aminodimethyl-aniline is condensed in pyridine solution with 1 mol. of p-nitrobenzoyl chloride. Dimethylsulphate is added to the condensation product

whereupon one reduces the nitro group to the amino group and the thus obtained intermediate product is condensed with chloride of cinnamic acid in presence of acid binding stuffs. It is also practicable and advantageous to condense 2 mols of the intermediate product by means of 1 mol. of phosgene or terephthaloylchloride in a pyridine solution.

If one substitutes a substantive basic dyestuff with one or more quaternary ammonium groups (cf. e. g. the German Patents 93,499 and 97,244) for the substantive ammonium base, one obtains the practicability of producing many different colour tones in combining both colours of the basic and of the acid dyestuff (cf. the following example).

If one chooses as acid dyestuff an after-chromatable one, the after-chromating can be done in a third bath or immediately in the acid dyeing bath.

Example 5

Cotton or viscose silk is brought at about 60° C. into a dyeing bath (bath-length 1:10 to 1:15), containing 2% of a substantive, basic dyestuff obtainable by the coupling of 2 mols of diazoo-
tized chloride of trimethyl-(n-aminophenyl-) ammonium with 1 mol. of bis-(2',3'-oxynaphtho- 
aryl)- benzidine in an alcoholic-alkaline solution. One dyes for 1 hour at 90–100°C. In adding 5 2% of acetic acid and 20% of common salt, then one cools down and rinses, whereupon the mate- 
rial is brought into a bath containing 2% of Congo-red in a bath-length of 1:15, wherein it is 
worked for about half an hour at boiling tem- 
perature. After that the bath will be nearly 
10 exhausted and one can rinse and dry. There results a bluish-red dyeing which is very fast to 
washing.

**Example 8**

Cotton is worked for 1 hour at 85°C. In a bath (in a bath-length of 1:15) containing 1% of the compound according to the following formula:

$$\text{CH}_2\text{CH} = \text{CH}-\text{CO-NH-}$$
$$\text{SO}_3\text{Na}$$

20

$$\text{NH}-\text{CO-CH}=\text{CH}-\text{CH}_3$$

25 further 1% of soda and 20% of sodium sulphate. Then one rinses cold, whereupon an after-treatment of half an hour takes place in a warm bath of 1% of the disazo dye-stuff of tetratozized 30 benzidine and 2-oxynaphthyl-7-trimethylammonium chloride (cf. German Patent 90,310), 2% of acrylic acid and 16% of common salt.

The above “acid and substantive mordant” is obtainable by condensing 1,5-naphtylenedia- 
mine-3,7-disulphonic acid sodium with the chloro- 35 ride of cinnamic acid in presence of an acid binding agent. It may be replaced with good results by the products which are obtained by the sul- 
phurizing of phenols (“katanol”).

**Example 7**

1% of the dye-stuff obtainable by the coupling of tetratozized dianisidine with 2-oxynaphthyl- 
7-trimethyl-ammonium chloride (cf. German Patent 90,310) jointly with 4% of the “substan- 
tive basic mordants” mentioned in Example 4, is 40 dyed on cotton or viscose silk as indicated there- 
in. An after-treatment takes place in a hot bath containing 2 g. of sodium laurylsulphonate per litre. The thus dyed material is of a soft and 45 agreeable handle.

Instead of the sodium lauryl-sulphonate one can likewise apply sodium cetly- or octadecyl- 
sulphonate or Turkey red oil or the sulphuric acid 50 ester salts of the dodecylo-, tetradecylo-, cetly- or 

cetadecyl-alcohol or compounds with similar properties such as oleytartain.

**Example 8**

One proceeds exactly as stated in Example 3 with the exception of employing diamine-brown 55 M (Schultz-Julius, l. c. Nr. 344) as acid direct 
dye-stuff. The violetblackish combination-dye- 
ing which is already rather fast to washing, has an 60 after-treatment to undergo for 25 minutes at 90–100°C. In a development bath with 1.5% of 
acetic acid, 15% of bichromate of potassium and 65 1.5% of copper vitriol in a bath-length of 1:15. The dyeing is then of a dark blue-black and 
eminent fast to washing and light.

**Example 9**

Cotton cloth is worked for 1 hour at 85°C. with 70

10% of a tannin extract of the pyrogallol- or eilagene tannic acid category such as myrobalan-, 
dividivi- or mango-leaves extract, in a bath- 
length of 1:15. Then one squeezes off and without 75 an intermediate rinsing; the material is brought 
into a development bath at 90°C. containing 70 2.5% of the disazoammonium base as per Example 
1, in a bath-length of 1:15. After digesting at 
80–100°C. until the ammonium base is com- 
pletely taken up one adds 5% of sodium bi- 
chromate and 2.5% of copper vitriol, then one 80 gently agitates for 20 minutes at 80–90°C. where- 
upon one cools and rinses. There results a 85 khaki-dyeing of an excellent fastness to light and 
washing.

**Example 10**

3% of the dye-stuff employed in Example 3 90 composed of diacetoxy toluo-sulphamine and 
naphtol are dyed on cotton while boiling for 95 about 30% of an hour and with an addition of 3% 
of acetic acid and 20% of common salt. Then one 
dissolves down to about 40°C. under continuous 100 agitation, at this temperature one adds 10% of 
tannin extract (myrobalan, dividivi, mango leaves 
extract) dissolved in a small amount of hot water, 
whereupon one heats to obtain re-boiling. After 
about half an hour one takes the cotton out of 
the bath and develops the dyeing for 25–30 minutes 
at 80–100°C. In a fresh bath containing 2% of 
bichromate of potassium, 3% of acetic acid and 105 2% of copper sulphate in a bath-length of 1:20. 
There results a dark bluish-black dyeing of an ex- 
cellent fastness to washing and light.

What I claim is:

1. A process for dyeing cellulosic fibres which 110 comprises producing on the fiber an insoluble salt of a substantive dye-stuff and a substantive 

quaternary ammonium base containing at least 
10 two quaternary ammonium groups and a system 
of no less than 8 conjugated non-interrupted 
115 double linkings in its molecule, whereby dyeings 

fast to washing are obtained.

2. A process for dyeing cellulosic fibres which 120 comprises dyeing the fiber by means of a substan- 
tive dye-stuff and after-treating the dyeing thus 

obtained with the solution of a substantive qua- 
125 ternary ammonium base containing at least two 
quaternary ammonium groups and a system of no 
less than 8 conjugated non-interrupted double 
130 linkings in its molecule, whereby dyeings fast 
to washing are obtained.

3. A process for dyeing cellulosic fibres which 135 comprises dyeing the fiber by means of a substan- 
tive dye-stuff and after-treating the dyeing 

thus obtained with the solution of a substantive 
140 disazotium base of the formula:

$$\text{N}_2\text{N}\begin{array}{c} \text{CH}_2\text{CH}_3 \\ \text{CH}_2\text{SO}_3 \end{array}$$

145 whereby dyeings fast to washing are obtained.

4. The process for dyeing cellulosic fibres which 150 comprises dyeing the fibre by means of a substan- 
tive dye-stuff and after-treating the dyeing thus 

obtained with the solution of an ammonium salt 
155 of the formula:

$$\text{CH}_3\text{CO} - \text{O} - \text{CO} - \text{NH} - \text{CH}_2\text{N}\begin{array}{c} \text{CH}_2\text{CO}_3 \end{array}$$

160 whereby dyeings fast to washing are obtained.

ERIK SCHIRM.