

# PATENT SPECIFICATION

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## (54) REACTIVELY DYED SUBSTRATE

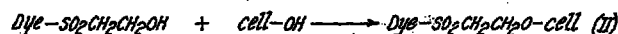
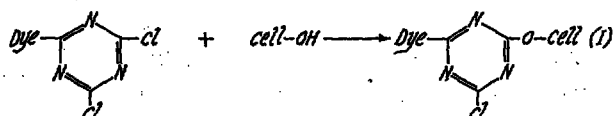
(71) We, BURLINGTON INDUSTRIES INC., a corporation organized and existing under the laws of the State of Delaware, United States of America, of 3330 West Friendly Avenue, Greensboro, North Carolina 27420, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to dyeing of fibres and more particularly to re-actively dyed fibres in which a chromophore is linked through a condensation residue to sites on the fibre.

Dyes are retained in fibres by physical adsorption, salt or metal-complex formation, solution, mechanical retention, or the formation of covalent chemical bonds. Physical adsorption and solution, in which the dye is partitioned between the fibre and the surrounding aqueous phase, are equilibrium reactions, and only by very careful selection of the dyes used can good washfastness properties be achieved. Salt and metal complex formation are also equilibrium reactions and, though generally the retention of the dye is favoured more than in physical adsorption, washfastness may still present a problem. The dyes that are held by mechanical retention (azoics, vats and sulfurs) are virtually insoluble in water and show excellent fastness to washing, but have other disadvantages. They are, for example, difficult and expensive to apply; loose dye, which is not easily washed off, may be deposited on the surface, resulting in low fastness to rubbing (crockfastness), and the final shade of the dyeing does not develop until completion of the whole dyeing cycle and after treatments.

Chemical bonding of dye to fibre for fixation of dye was recognized as early as 1895. The reactive dye systems currently available require that the dyes contain a functional group capable of forming a covalent chemical bond with the fibre.

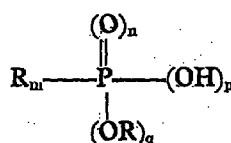
Fibre-reactive dyes are used quite widely in colouring cellulose and proteinaceous fibres. They, of course, exhibit excellent washfastness, resistance to rubbing, tinctorial powers, ease of application and levelling. The latter quality is a measure of uniformity and most important for long dye runs and colour matching. Inasmuch as one can prepare either fibre substantive or non-substantive dyes, direct application to precision printing becomes a feasible and functional commercial operation. The reaction of the dye with cellulosic fibres is basically an etherification reaction and is broadly represented as:



The triazine reactive group imparts oil-solubility characteristics to the high-molecular-weight dye which hinders and interferes with an aqueous solubilizing group such as —SO<sub>3</sub>H. These dyes are unstable and it is difficult to work with them. Most

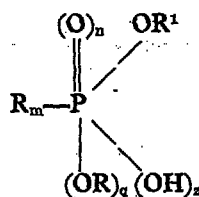
of the reactive dye systems are based upon chemistry where the reaction is effected in alkaline solutions. There is no present reactive dye system which operates effectively in an acid pH. Such a system is desirable in the dyeing of mixed fabrics such as cotton blends with polyester, wool or nylon, the latter fibres being dyeable by acid dyes. However, acid dyes generally have no affinity for cellulose and usually only find use in dyeing of proteinaceous fibers. Furthermore, since the dye and fibre substrate are co-reactive, complete dyeing of the fabric will occur unless special precautions are practised to localize the dye in areas of the fabric by printing, stencilling or other graphic technique.

In accordance with the present invention, a reactively dyed hydroxy-substituted organic polymeric substrate is formed by contacting a substrate of the formula  $R'OH$ , where  $R'$  is the chain of the polymer and  $OH$  is any hydroxyl group on the chain, in the presence of a carbodiimide with a chromophore-substituted phosphorus acid of the formula:



(A)

where  $R$  is the chromophore,  $m$  is 0, 1 or 2,  $n$  is 0 or 1,  $p$  is 1 or 2,  $q$  is 0 or 1,  $m+q$  is not 0 and  $m+2n+p+q$  is 3 or 5 (preferably 5), and heating the contacted substrate to a temperature of at least 200°F for a time sufficient to form a dyed substrate. The invention also provides a reactively dyed hydroxy-substituted substrate having a phosphorus ester linkage between the chromophore and chain and having the formula:



(B)

where  $z$  is  $p-1$  and  $R$ ,  $R'$ ,  $m$ ,  $n$  and  $q$  are as defined above. Preferably  $m=n=z=1$  and  $q=0$ .

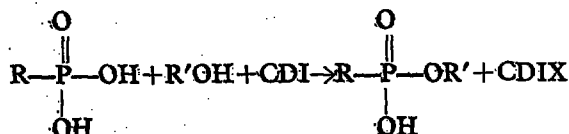
The invention further provides a composition for reactively dyeing hydroxy-substituted organic polymeric substrates comprising an aqueous solution containing at least 0.1% by weight of a chromophore-substituted phosphorus acid, preferably having the formula (A) above, or an amine or ammonium salt thereof, and a water-soluble carbodiimide in which the ratio equivalent of carbodiimide to acid is at least 2:1.

The dye system of the present invention can be used in acidic to mildly alkaline solutions. It is a reactive system in which the reactive function is not self-contained in the dye molecule. Since the dye and fibre require the presence of a condensation agent for reaction, certain dyes such as azo dyes, where the dye is formed by a simple coupling reaction, can be formed via an intermediate on the fabric which can be selectively colour-developed in discrete locations to form a pattern. The background areas can be fixed to expose or decompose the remaining precursor areas. The dye system of the invention is further simplified in that a single group serves both as an aqueous solubilizing group and as the potentially reactive coupling site to the fibre, thus providing a more simplified synthesis and a less complex and more stable dye molecule and dyed fabric.

The dye system of the invention results in reactively dyed fabrics by immobilization of a dye as a cellulose phosphorus ester.

Thus, a chromophoric grouping ( $R$ ) linked chemically to a phosphorus acid such as a phosphonic, phosphinous, phosphinic or phosphoric acid, reactively dyes cellulose ( $R'OH$ ) with the aid of a carbodiimide condensing agent (CDI). Cyanamide, which is a suitable carbodiimide, allows for a rapid esterification of phosphorus acids with alcohols. The by-product, CDIX, is urea. Thus, where  $R$  is a chromophore and  $R'OH$  is cellulose, a fibre-reacted dye compound is formed with cellulose. This results

in a substantial and washfast dyeing of cotton and other cellulosic or hydroxy-containing substrates. Cellulose esters of phosphonic acid dyes are found to be the most stable to heavy-duty alkaline detergents. The reaction of phosphonic acid dyes is considered to proceed as follows:



The fabric or fibre system of the invention proceeds by forming an aqueous solution of a chromophore or precursor thereof linked chemically to a phosphorus-containing acid. The solution generally contains at least 0.1% of the dye and generally no more than 10% by weight of the dye depending on the intensity of the chromophore and the shade desired. The dye concentration is generally between 0.1 and 5% by weight and the concentration of reacted dye on the fabric is believed to be in the range of 0.01 to 0.5 weight percent;  $10^{-4}$  to  $10^{-2}$  mol. percent.

The pH of the solution is generally 3—4 but can be varied from 1.5 to 9. Lower pHs (i.e. below 3) can be provided by addition to the impregnation bath of 1—5% of an acid which is non-volatile at the cure temperature and does not cause undue degradation of the substrate. Such acids include phosphoric acids, alkyl phosphonic acids and chloroacetic acid. This appears to improve the efficiency of the dye immobilization since less dye is found to wash out after cure. The amount of carbodiimide is usually increased in a bath containing added acid. Baths of pHs above 2 may be utilized containing salt which are converted to the acid form during cure such as volatile amine salts or ammonium salts of the phosphorus acid chromophore. Higher pH baths may be necessary in certain situations which present corrosion problems, mixed fibre systems or fibres which would be excessively degraded at low pH.

Generally, in the bath the equivalent ratio of the diimide to the phosphono function is at least 2:1. Curing is generally conducted at a temperature of at least 200°F and generally below 400°F. Optionally, the fabric may be preliminarily dried at a temperature below 200°F before cure. The cure time can be varied from the order of seconds to hours depending on the temperature, dye concentration and fibre being coloured.

The reactive dye system of the invention is generally applicable to substrates containing available hydroxyl groups such as cellulose, particularly cotton, and may be practised on fibres, films, yarns, cords, threads, paper and fabrics, which may be non-woven, woven, knitted, or other types including pile fabrics, velvets, corded webs or webs formed by a random webber.

The water-soluble condensation agent assists in the formation of the ester linkage between the chromophore, R, and the cellulose substrate, R'OH. The agent is preferably a water-soluble carbodiimide such as cyanamide or dicyandiamide.

The impregnating bath may also contain minor amounts of conventional additives or assistants such as anti-migrating agents such as Glauber's salt, or wetting agents. Compatible thickeners may also be present.

The dyes that can be utilized in the dye immobilization process of the invention can be of diverse type and structure. The dye may be an anthraquinone, phthalocyanine, mono-azo, polyazo, bezanthrone, pyrazolone, naphthaquinone, triaryl-methane or cyanine type that is modified to contain a phosphorus acid group to impart water-solubility and to provide a reactive site for attachment to the hydroxyl atoms on the substrate. The dyes may contain other aqueous solubilizing groups such as sulphonate and may contain other substituents that do not interfere with aqueous solubility characteristics or the dye immobilization esterification reaction.

Many of the phosphorus-acid-substituted dyes utilized in the process of the invention are known readily available materials and have been used to direct dye wool and other proteinaceous fibres. Suitable dyes are disclosed in Belgian Patent No. 570,326, U.K. Patent No. 455,092 and United States Patent Nos. 2,596,660 and 2,799,701. Analogues of sulphonated dyes can readily be synthesized in the phosphono form by substituting the phosphono analogue for the sulphono-containing compound during synthesis.

The process of the invention may be readily adapted so that it can be carried out in commercially available machinery used for dyeing or textile printing processes and for continuous or non-continuous variations of such processes. The fibrous or sheet material may be impregnated with the dye-stuff solution and then subjected

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to curing by heating, for example, in a hot flue dryer, an oven or a stentor. The impregnation may be carried out for example by padding material with an aqueous solution containing the dyestuff and curing agent. The dye treatment may also be carried out by textile printing methods, for example, by locally treating the textile with a solution containing the dyestuff and condensation agent and thereafter subjecting the printing material to an elevated temperature for curing. Alternatively a phosphono-substituted primary agent may be coupled to the cellulose and thereafter coupled to an azo chromophore component.

Dye systems of the present invention provide a further advantage since the dye can be recovered from the bath by precipitation on a calcium substrate such as lime,  $\text{CaCO}_3$  or marble and can be regenerated by acid.

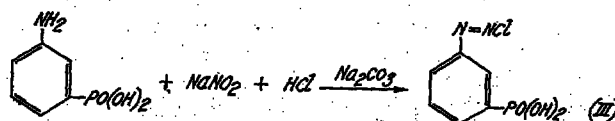
The invention will now become better understood by reference to the following detailed illustrative Examples. The words "Triton" and "Cellosize" are trade marks.

#### Example 1

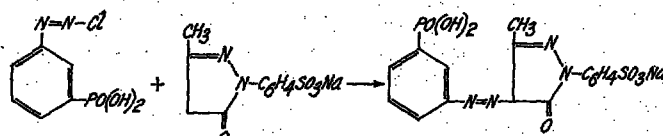
The following example illustrates the synthesis of a phosphono analogue of Yellow No. 1, a pyrazolone dye:

8.7 grams of 3-phosphanilic acid and 5.3 g of  $\text{Na}_2\text{CO}_3$  were added to 100 ml of  $\text{H}_2\text{O}$  and cooled to  $15^\circ\text{C}$ . 3.7 g of  $\text{NaNO}_2$  in 10 ml of  $\text{H}_2\text{O}$  was added to yield a brown solution which was slowly poured with stirring onto 21 ml of concentrated  $\text{HCl}$  containing 60 g of ice. The mixture was stirred for fifteen minutes and gave a positive response to the starch-KI test.

The diazotisation method is based on Vogel, "Practical Organic Chemistry" (1951), p. 596, the disclosure of which is incorporated herein by reference, and follows the following reaction sequence:



Coupling of the diazotized intermediate (III) is based on U.K. Patent No. 753,771. The solution containing the intermediate (III) was added to a solution containing 12.7 g (1/20 mole) of 3-methyl-1-(p-sulphophenyl)-2-pyrazol-5-one and 10 g of sodium acetate in 100 ml of  $\text{H}_2\text{O}$ . The pH of the second solution had been adjusted from 5.3 to 7.0 with  $\text{NaOH}$ . After stirring for fifteen minutes the pH was 2.0 and there was no evidence of precipitation. On addition of isopropanol, a yellow powder was precipitated which after separation and drying in a vacuum oven yielded 13 g. Coupling proceeded according to the following reaction:

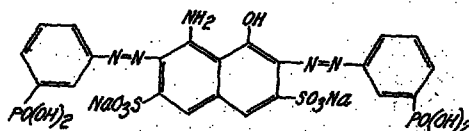


#### Example 2

The following example illustrates the synthesis of a bis-phosphono bis-azo dye. 3-phosphanilic acid was diazotized according to the procedure of Example 1 using 13 ml of concentrated  $\text{HCl}$ . 18.0 g (0.05 mole) of the mono-sodium salt of 8-amino-1-naphthol-3,6-disulfonic acid was suspended in 50 ml of  $\text{H}_2\text{O}$  and the pH was adjusted from 2.3 to 7 with  $\text{NaOH}$ . This solution was added to the diazotate to form a dark-red solution having a pH of 2.5.

Alkaline coupling was practised according to Vogel, *supra*, p. 597.

The red solution precipitated on standing and was adjusted to pH 7 with  $\text{NaOH}$ . 40 ml of a 10%  $\text{NaOH}$  solution was then added and cooled to  $5^\circ\text{C}$ . A second preparation of diazotate was then added to form a blue solution having a pH of 7.4. After fifteen minutes the pH was adjusted to a pH of 2 with  $\text{HCl}$ . The dye was precipitated with isopropanol to yield 40 grams of black powder having the formula:



### Example 3

The pyrazolone yellow dye of Example 1 was used to dye cotton fabrics according to the following procedure.

A pad bath was prepared containing 5% of the pyrazolone yellow dye, three equivalents of cyanamide (1.33 weight percent) and 0.1% of the non-ionic wetting agent sold under the trade mark Triton X 100 (octyl phenoxy polyethoxy ethanol). The bath had a pH of 2.9. Samples of print cloth fabric were padded at 40 psi, and then oven-dried for five minutes at 150°F except for one fabric that was air-dried at room temperature. One sample of fabric was cured for five minutes at 320°F. An oven-dried fabric was cut in half for colour comparison. All but one half of the oven-dried fabric was washed for eight minutes with heavy-duty detergent, dried and then ironed. The air-dried fabric was colourless and the oven-dried fabric was colourless, whereas the cured fabric had a bright lemon yellow colour with some washoff by comparison with unwashed. The coloured fabrics were boiled for one hour in 3%  $K_2CO_3$  with some colour lost. The final colour was a pastel yellow shade of the original bright yellow colour.

Since the fabric subjected to air drying lost all colour on washing, it is apparent that the dye was not substantive. It is quite unexpected that the ester linkage of the fixed dye is stable to hot detergent alkaline medium since it would be expected that the phosphorus ester residue would be hydrolysed and rupture the dye attachment.

### Example 4

The blue dye of Example 2 was used to colour cotton fabric according to the following procedure:

A pad bath was prepared containing 5% of the blue dye plus 6 equivalents of cyanamide (1.73%) and 0.1% of Triton X 100. The pH of the bath was 2.6. Samples of cotton fabric were treated, dried and cured as in Example 3. After washing, the air-dried fabric was almost colourless. The oven-dried fabric was a very pale blue whereas the cured fabric was a very dark navy blue. There was some slight washoff by comparison with the unwashed fabric. The warp shrinkage was -3.75% whereas the fill shrinkage was +0.75%. After the fabric was boiled for one hour in 3%  $K_2CO_3$ , the final colour was a dark purple.

### Example 5

An attempt was made to fix the dye of Example 1 on fabric using heat without the presence of a carbodiimide.

A bath was prepared containing 5% by weight of the pyrazolone yellow dye of Example 1 plus 0.1% Triton X 100. The pH of the bath was 2.9. The bath did not contain any carbodiimide or equivalent material.

Samples of cotton fabric were padded at 40 psi, dried for five minutes at 150°F and cured for five further minutes at 320°F, washed in heavy-duty detergent and ironed. The fabrics contained only a trace of yellow colour. A dye and heat step at curing temperature is not capable of fixing the dye on the fabric.

### Example 6

An attempt was made to fix on fabric the dye of Example 1 by means of a pad bath containing urea.

A bath was prepared containing 5% by weight of the pyrazolone yellow dye of Example 1, 0.1% Triton X 100 and 1.9% urea (3 equivalents). The pH of the bath was 2.9.

Samples of cotton fabric were treated as in Example 5 and the samples retained no more colour than those of Example 5 showing that no dye immobilization occurred by this procedure.

### Example 7

An attempt was made to fix the dye of Example 2 on fabric using heat or urea in the absence of a carbodiimide.

Two baths were prepared, one containing 5% of the blue dye of Example 2 plus 0.1% Triton X 100 and the other additionally containing 2.5% urea (6 equivalents). The pH of the first bath was 2.65 and that of the second bath with urea was 2.70. Samples of cotton fabric were padded at 40 psi, dried for five minutes at 150°F, cured for five minutes at 320°F, washed in heavy-duty detergent and ironed. Only a trace of blue remained in the fabrics. Colours were all about the same.

### Example 8

The following example shows the use of polyvinyl alcohol and phosphoric acid as adjuvants to the colouring bath:

5 A pad bath was prepared containing 1% by weight of the blue dye of Example 2, 1%  $H_3PO_4$ , 1.6% cyanamide and 6 milliliters of 4% polyvinyl alcohol. No wetting agent was added. The pad bath was used to treat 100% cotton cloth and 50—50 cotton polyester cloth, according to the procedure of Example 3. The cloths showed good colour retention and stability with very little washoff and very good resistance to boiling  $K_2CO_3$ . A similar bath containing 4% Cellosize in place of polyvinyl alcohol gave a similar result and also imparted some blue colour to glass cloth.

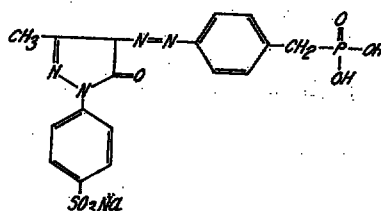
### Example 9

The following example illustrates the use of dicyandiamide in place of cyanamide. A pad bath was prepared containing 1.5% by weight of the yellow dye of Example 1 and 1% of dicyandiamide. (0.8% would be a ratio of 1:3). Samples of cotton cloth were treated according to the procedure of Example 3. After washing, the dye immobilization was essentially the same as the cyanamide-treated fabrics of Example 3.

### Example 10

The following example illustrates preparation of the benzyl phosphonic analogue of the dye of Example 1.

*p*-Aminobenzyl phosphonic acid was coupled with the sulfophenyl pyrazolone of Example 1 using 9.4 g of the benzyl acid (0.1 mole) in place of 8.7 g of the phenyl acid. The pH was finally adjusted to 3.0 with HCl and the solid precipitated with isopropanol, presumably as the monosodium salt having the structural formula:



The dye exhibited similar behaviour when utilized to colour cotton fabric samples according to the procedure of Example 3.

### Example 11

The following experiment illustrates the preparation and use of the ammonium salt of the dye of Example 1 at higher pH.

An ammonium salt of the yellow dye of Example 1 was prepared by dissolving the dye in an aqueous  $NH_4OH$  solution and evaporation the solution to dryness.

A pad bath was prepared containing 1% of the ammonium salt dye, 0.3% cyanamide and 0.25% Alipal CO 436 (nonyl phenoxy polyethoxy ethanol-sulfated,  $NH_4^+$  salt). The pH of the bath was 5.8. The bath was applied to fabric and cured as in Example 3. The dye immobilization was substantially the same as in Example 3.

### Example 12

An acid pad bath was prepared containing 1% of the sodium salt of the phenyl dye of Example 1, 0.25% of Alipal and 3% of  $H_3PO_4$  and 4.5% of cyanamide which represented an equivalent ratio of (1:3) of the cyanamide to the dye and acid. The pH of the pad bath was 1.8.

Samples of fabric cloth impregnated, cured and washed according to the procedure of Example 3 showed very little washoff. U.V. analysis of the cloth indicated about 75% dye fixation.

### Example 13

Methyl phosphonic acid (MPA) was substituted for the  $H_3PO_4$  of Example 12 and the cyanamide content was reduced by 1.3% to adjust the MPA/cyanamide equivalent ratio to 1:2. The pH of the bath was 1.8. Samples of fabric, impregnated, cured and washed according to the procedure of Example 3 again demonstrated very little washoff. A sample of fabric which was air-dried before cure to minimize migration showed somewhat improved colour retention.

## Example 14

The following experiment shows the necessity of a phosphorus acid group in the dye molecule.

A pyrazolone dye was prepared utilizing *m*-sulphanilic acid in place of the *m*-phosphanilic acid of Example 1. A bath was prepared containing 1% of the sulphonated dye, 3%  $H_3PO_4$ , 0.25% Alipal and 4.5% cyanamide. The pH of the bath was 1.75. Samples of fabric impregnated, cured and washed according to the procedure of Example 3 showed extreme washoff demonstrating that little or no dye was fixed.

Fixation and immobilization of dye by formation of a phosphorus acid ester linkage was further confirmed by the following experiment.

## Example 15

A solution of 5% *m*-phosphanilic acid containing 3 equivalents of cyanamide was used to impregnate cotton cloth. The cloth was cured at 320°F for five minutes to couple the amine base to the cellulose through the phosphono-linkage.

The cellulose-coupled amine base was then subjected to diazotization with the  $NaNO_2$ -HCl solution of Example 1 to form a diazonium salt. A portion of the cloth was exposed to light to decompose the diazonium salt. The fabric was then immersed in a solution of the sulfophenyl pyrazolone utilized in Example 1 and dried and washed. Colour was retained only in the nonexposed areas, confirming the phosphono-ester linkage as the immobilization mechanism.

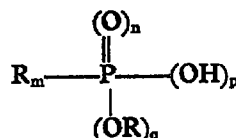
## Example 16

A copper phthalocyanine substituted with phosphonic acid and sulfonic acid groups was prepared by heating an intimate mixture of triammonium 4-sulfophthalic acid (11 g), monopotassium 4-phosphonophthalate (11 g), urea (20 g), cupric chloride dihydrate (3 g), and ammonium molybdate (0.25 g) at 250°C. The product was purified by washing with hydrochloric acid and drying in a vacuum oven at 60°C.

A bath was prepared containing 1% of this product, 1%  $H_3PO_4$ , 4.4% cyanamide and 0.25% Alipal. The pH of the bath was adjusted to 2.5 with triethanolamine. Samples of fabric impregnated, cured and washed according to the procedure of Example 3 were a greenish-blue colour.

## WHAT WE CLAIM IS:—

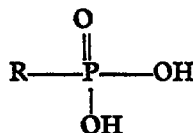
1. A method of forming a reactively dyed hydroxy-substituted organic polymeric substrate comprising contacting a substrate of the formula  $R'OH$ , where  $R'$  is the chain of the polymer and OH is any hydroxyl group on the chain, in the presence of a carbodiimide with a chromophore-substituted phosphorus acid of the formula:



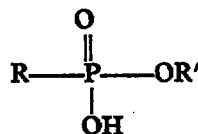
where R is the chromophore,  $m$  is 0, 1 or 2,  $n$  is 0 or 1,  $p$  is 1 or 2,  $q$  is 0 or 1,  $m+q$  is not 0 and  $m+2n+p+q$  is 3 or 5; and heating the contacted substrate to a temperature of at least 200°F for a time sufficient to form a dyed substrate.

2. A method according to Claim 1 in which  $m+2n+p+q=5$ .

3. A method according to Claim 2 in which the acid is a phosphonic acid of the formula:



and the dyed substrate is a material of the formula:



where R and  $R'$  are as defined in Claim 1.



\* C L M S \*

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## Example 14

The following experiment shows the necessity of a phosphorus acid group in the dye molecule.

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Fixation and immobilization of dye by formation of a phosphorus acid ester linkage was further confirmed by the following experiment.

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A solution of 5% *m*-phosphanilic acid containing 3 equivalents of cyanamide was used to impregnate cotton cloth. The cloth was cured at 320°F for five minutes to couple the amine base to the cellulose through the phosphono-linkage.

The cellulose-coupled amine base was then subjected to diazotization with the  $NaNO_2$ -HCl solution of Example 1 to form a diazonium salt. A portion of the cloth was exposed to light to decompose the diazonium salt. The fabric was then immersed in a solution of the sulfophenyl pyrazolone utilized in Example 1 and dried and washed. Colour was retained only in the nonexposed areas, confirming the phosphono-ester linkage as the immobilization mechanism.

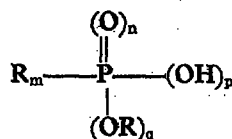
## Example 16

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A bath was prepared containing 1% of this product, 1%  $H_3PO_4$ , 4.4% cyanamide and 0.25% Alipal. The pH of the bath was adjusted to 2.5 with triethanolamine. Samples of fabric impregnated, cured and washed according to the procedure of Example 3 were a greenish-blue colour.

## WHAT WE CLAIM IS:—

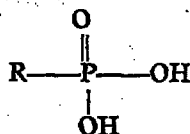
1. A method of forming a reactively dyed hydroxy-substituted organic polymeric substrate comprising contacting a substrate of the formula  $R'OH$ , where  $R'$  is the chain of the polymer and OH is any hydroxyl group on the chain, in the presence of a carbodiimide with a chromophore-substituted phosphorus acid of the formula:



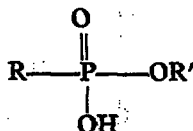
where  $R$  is the chromophore,  $m$  is 0, 1 or 2,  $n$  is 0 or 1,  $p$  is 1 or 2,  $q$  is 0 or 1,  $m+q$  is not 0 and  $m+2n+p+q$  is 3 or 5; and heating the contacted substrate to a temperature of at least 200°F for a time sufficient to form a dyed substrate.

2. A method according to Claim 1 in which  $m+2n+p+q=5$ .

3. A method according to Claim 2 in which the acid is a phosphonic acid of the formula:



and the dyed substrate is a material of the formula:



where  $R$  and  $R'$  are as defined in Claim 1.



4. A method according to Claim 2 in which the acid is a chromophore-substituted phosphonic, phosphinic, phosphonous or phosphoric acid.

5. A method according to any one of Claims 1 to 4 in which the substrate is in fibrous form.

5 6. A method according to Claim 5 in which R'OH is cellulose.

7. A method according to any preceding claim in which the substrate is contacted by impregnating the material with an aqueous solution containing at least 0.1% by weight of the chromophore-substituted phosphorus acid.

10 8. A method according to Claim 4 in which the solution contains from 0.1% to 5% by weight of the acid.

9. A method according to any one of Claims 1 to 8 in which the carbodiimide is a water-soluble carbodiimide and the equivalent ratio of carbodiimide to chromophore-substituted acid is at least 2:1.

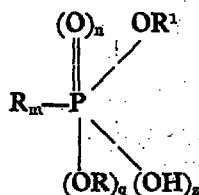
15 10. A method according to any one of Claims 1 to 9 in which the pH of the solution is from 1.5 to 9.

11. A method according to Claim 10 in which the pH of the solution is adjusted to below 3 by adding from 1—5% by weight of an acid to the solution.

20 12. A method according to Claim 10 in which the pH of the solution is above 2 and the chromophore-substituted acid is in the form of a salt with a volatile amine or ammonium.

13. A method according to any one of Claims 1 to 12 in which the chromophore is anthraquinone, phthalocyanine, monoazo, polyazo, benzanthrone, pyrazolone, naphthaquinone, triarylmethane or cyanine.

25 14. A reactively dyed hydroxy-substituted organic polymeric substrate of the formula:



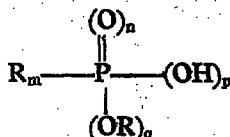
where R, R', m, n and q are as defined in Claim 1 and z is p-1.

30 15. A substrate according to Claim 14 in which R' is the residue of a cellulosic chain.

16. A substrate according to Claim 15 in which m is 1, n is 1, z is 1 and q is 0 and the chromophore is anthraquinone, phthalocyanine, monoazo, polyazo, benzanthrone, pyrazolone, naphthaquinone, triarylmethane or cyanine.

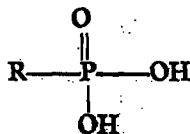
35 17. A composition for reactively dyeing hydroxy-substituted organic polymeric substrates comprising an aqueous solution containing at least 0.1% by weight of a chromophore-substituted phosphorus acid or an amine or ammonium salt thereof and a water-soluble carbodiimide in which the ratio equivalent of carbodiimide to acid is at least 2:1.

18. A composition according to Claim 17 in which the acid is a material of the formula:



where R, m, n, p and q are as defined in Claim 1.

19. A composition according to Claim 18 in which the acid is a phosphonic acid of the formula:



45 where R is as defined in Claim 1.



20. A composition according to Claim 19 further including 1—5% by weight of a phosphoric acid, an alkyl phosphonic acid or chloroacetic acid.

21. A method according to Claim 1, substantially as hereinbefore described in any one of the foregoing Examples.

22. A reactively dyed hydroxy-substituted organic polymeric substrate when prepared by a method according to any one of Claims 1—13 and 21.

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