(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: **0 442 749 A2**

(12) # EUROPEAN PATENT APPLICATION

(21) Application number: **91301218.3**

(22) Date of filing: **14.02.91**

(51) Int. Cl.[5]: **D06P 1/647**, D06M 13/342, D06M 13/224, D06P 1/651

(30) Priority: **14.02.90 GB 9003367**

(43) Date of publication of application: **21.08.91 Bulletin 91/34**

(84) Designated Contracting States: **BE CH DE FR GB IT LI LU NL SE**

(71) Applicant: **BP Chemicals Limited**
Belgrave House 76 Buckingham Palace Road
London, SW1W 0SU (GB)

(72) Inventor: **Black, Brian David, BP Chemicals Limited**
Salt End
Hull, HU12 8DS (GB)

(74) Representative: **Krishnan, Suryanarayana Kalyana et al**
BP INTERNATIONAL LIMITED Patents & Agreements Division Chertsey Road
Sunbury-on-Thames Middlesex TW16 7LN (GB)

(54) **Textile processing acidulants.**

(57) This invention relates to an acidulant for regulating the pH in textile processing. The acidulant comprises a mixture of triacetin and one or more esters of dibasic acids, the acidulant being substantially free of C_1-C_3 alkyl acetates.

EP 0 442 749 A2

TEXTILE PROCESSING ACIDULANTS

The present invention relates to the use of mixed esters as additives in textile processing, especially in the dyeing and printing processes for natural and synthetic fibres and fabrics.

In the dyeing industry organic acids and their salts are commonly used as acidulants in the dyeing of wool, nylon, paper, leather and other natural and synthetic fibres with certain acid and chrome dyes. Organic acids such as citric acid and acetic acid are also used as components of printing pastes e.g. for printing carpets and in printing processes. The use of such acids and salts is disclosed for example in French Patent Application No. 2240317, German Patent Nos C-317725 and C-874291 and in GB-A-1048482. These acids and their salts perform several functions in the dyeing and printing processes such as :-

- to ensure economic exhaustion (defined as the degree of uptake of the dye by the material dyed) from the aqueous dye bath, to prevent oxidation of the dyestuff by dichromate in the case of certain chrome dyes by the reducing action of acids such as formic acid,
- to achieve rapid dyeing of wool by padding (immersing and then nipping) wool fabric with a concentrated solution of the dye in formic acid,
- to achieve and maintain the desired pH conditions for the printing of wool and other fabrics, and
- to achieve adequate levelling (evenness or uniformity of dyeing) with certain dyes, e.g. mordant acid dye and premetallised dye wherein the acid is used in the form of its neutral salt for the buffering effect to maintain a constant PH.

In all the above applications, the use of free organic acids as acidulants presents three main problems. Firstly, the intermittent addition of free acid into the system causes a sudden upsurge of acidity in the system at the time of addition thereby impairing the quality of dyeing. Secondly, this makes it difficult to obtain levelled dyeing because effective pH control of the system cannot be achieved. Where a pH swing method is being used, e.g. in the winch dyeing of nylon apparels, it may be necessary to use expensive metering equipment to add pH control agents. Thirdly, the use of free organic acids presents handling problems due to the disagreeable odours of the acid fumes, the need to wear protective clothing and the corrosion of equipment and machinery exposed to such acids and fumes.

It is therefore necessary to ensure that the acidulant used results in a gradual shift of the dyebath pH from alkaline to acid. If this can be achieved, stages in textile processing such as the dyeing process can be initiated in an alkaline or neutral medium and will offer the optimum conditions for uniform distribution and exhaustion of the dye to ensure very level dyeings and to minimise the dyeing cycle time. At the same time it will be advantageous if the use of free acids can be avoided so as to minimise problems of corrosion and handling.

The problem has to some extent been solved by the use of proprietary esters such as diacetin and acetyl trimethyl citrate. Both these release the acid "in situ" by hydrolysis under the dyeing conditions and thereby offset the handling problems. Examples of processes in which these acidulants are used include (a) dyeing polyamides (nylon apparels) (pH 3.5-6.0) or (b) dyeing wool (pH 4.0-6.0). The proprietary esters used hitherto, are, however, not cost-effective.

It has now been found that, by replacing conventional organic acids or proprietary esters either wholly or partially by a mixture of esters according to the present invention, compositions are formed which regulate the pH e.g. of the dye bath so as to obtain adequate levelling and exhaustion of dyes while fluctuations, odour and corrosivity of the free acids. The use of these mixed esters in textile processing not only minimise the problems relating to odour and corrosivity but also has the surprising advantage of eliminating the need in some cases for separate buffering agents.

Accordingly, the present invention is an acidulant for regulating pH in textile processing characterised in that the acidulant comprises a mixture of triacetin and one or more esters of dibasic acids, said acidulant being substantially free of C_1-C_3 alkyl acetates.

The acidulant mixture of the present invention can wholly or partially replace acidulants conventionally used for regulating pH during textile processing. For instance, the mixture of triacetin and dibasic acid esters may be used as such or in combination with other esters such as glycol mono- and di-formates, glycol mono- and di-acetates, diacetin, or with free C_1-C_3 monocarboxylic acids. The dibasic acid ester used may be suitably selected from the C_1-C_4 alkyl esters of one or more saturated aliphatic dibasic acids having from 2-12 carbon atoms, preferably from 2-8 carbon atoms. Esters of oxalic, succinic, glutaric and adipic acids are preferred and dimethyl esters of these dibasic acids are most preferred. Mixed esters of succinic, glutaric and adipic acid esters (commonly also known as the 'nylonate esters') are particularly preferred. In such a mixture, in which the esters are usually in the form of their dimethyl esters, the specific esters are present in the following ranges of concentration in % w/w :

Dimethyl succinate - 15-25

Dimethyl glutarate - 55-65
Dimethyl adipate - 12-23

In the acidulants of the present invention, the triacetin is suitably present in an amount from 25-95% w/w, preferably from 50-85% w/w of the total acidulant. It is a feature of the invention that the combination of triacetin and the dibasic acid ester shows synergy when used as an acidulant because the mixture of these two compounds shows a lower pH value than is obtainable with the individual components.

The ester mixture can be incorporated at various points during textile processing, for example at one or more of the stages of scouring of the fabric, bleaching, chlorination, dyeing, mordanting, levelling, exhaustion, fixing, printing, finishing, water-proofing and milling. These terms are well known in the art and are defined in standard text books such as for example, "Textile Auxiliaries", by Batty, J.W., Pergamon Press (1967) and "The Theory and Practice of Wool Dyeing" by Bird, C.L. published by the Society of Dyers and Colourists, Bradford, Yorkshire (1963), 3rd Edition.

Typically, in the dyeing of wool the machine is loaded with wool and water is added together with the ester mixture which wholly or partially replace the conventional acids (e.g. formic acid, acetic acid) normally used, the levelling agents and pH control agents (e.g. sodium and ammonium sulphate). In certain instances additional pH control agents can be omitted because the ester mixture avoids wide fluctuations of pH thus also performing a buffering function. The dye bath is held at 40°C for 5-30 minutes, the dye is added and the bath raised to the boil in 45-60 minutes. The dye bath is held at the boil for 30-60 minutes. At this stage more ester mixture can be added, if necessary, to maintain the pH and to complete dye exhaustion. In such dyeing processes the ester mixture used in the present invention may be added with the initial charge of water to replace either the conventional acidulants or the levelling agent or both. The concentration used (on a 100% basis) may be in the range of 0.05-5% w/w based on the weight of the liquor being used in the dye bath. The ester mixture may be added as such or as solutions of the esters in a solvent. Additionally, the solutions can be used as a solvent carrier for the dyes.

In dyeing or printing paper, the control of pH is essential and the ester mixture used in the present invention not only enables such control but also can be added to the dye used for colouring the pulp or the final product paper.

The ester mixture may be used in the present invention in conjunction with other conventional assistants or agents such as for example wetting agents, anti-foaming agents, solubilising agents and thickeners, used in the dyeing or printing process.

It may sometimes be advantageous to add to the dye bath a co-solvent such as a glycol or a glycol ether, eg an alkyl diglycol ether such as butyl diglycol ether, to aid the dispersion of the components in the bath, especially if such components are prediluted with water prior to introduction into the dye bath.

The types of dyes used are not limited by the process of the present invention. For example the dyes may be acid, azoic, basic, direct, indirect, dispersed, reactive, mordant, premetallised, solvent, sulphur, vat dyes and optical brightners.

The principal advantages of using the ester mixture during textile processing are as follows :-

– pH control in the dyeing process to achieve gradual change of pH from an alkaline or neutral to acidic pH values thereby allowing good levelling and exhaustion to be achieved.

– It is less volatile than conventional compositions containing the free organic acids (e.g. formic acid, acetic acid).

– Solutions of the ester mixture will act as buffer systems thereby preventing sudden upsurge in the pH value of the dye bath when fresh amounts of the ester are added either alone or together with free acid. This enables achievement of a controlled reduction in pH of the bath thereby eliminating in some cases, the need for a buffering agent.

– Where a pH swing method is used e.g. in which dyeing of nylon apparels, no expensive metering equipment is needed to add to the ester mixture which is the pH control agent.

– It is less corrosive to skin, clothing, plastics and metal and hence are safer to the operator and do not promote deterioration of equipment.

– Typically the ester mixture is more cost effective than other proprietary esters now in use.

– The use of the esters in the mixture result in shorter dyeing times.

– The ester mixture is particularly suited for the dyeing of nylon apparels.

Moreover, the pH profile of the mixture is such that the relatively low pH value is attained rather gradually - which is what is desired in a dye bath - and there is a sudden dip in the pH value when it nears its final value. This is a very significant advantage because it is sometimes necessary to add supplementary aliquots of acid at the end of a dyeing cycle in order to ensure complete exhaustion. The use of the acidulant of the present invention mitigates the problem of adding supplementary acids.

The present invention is further illustrated with reference to the following Examples.

Examples

The following simple tests were performed as control tests (without any dye) to test the ability of the ester mixture to gradually regulate the pH from a neutral/alkaline medium to acid.

In the Examples the following abbreviations have been used :-

DBE - Mixture of dimethyl esters of succinic, glutaric and adipic acid as specified above.

Triacetin - glycerol triacetate

BDGE - butyl diglycol ether

5 l of distilled water was added to a 5 litre beaker fitted with a heater and temperature controller. The water was allowed to equilibrate to 50°C and its pH adjusted to ca pH 8.5 using 25% ammonia solution (1 drop), 5g of the potential acidulant was then added and the initial pH noted. The temperature of the solution was maintained at 50°C for 10 minutes and then increased at a rate of 1°C per minute to 95°C, its pH being recorded every 5 minutes. The temperature was then maintained at 95 to 98°C for 40 minutes whilst continuing to record the pH every 5 minutes.

The solution was stirred continuously throughout the test.

A pH vs time plot was drawn to show the pH reducing profile of the potential acidulant during a typical dyeing cycle. The results are tabulated below.

The results below show that although the individual esters in the mixture when used alone do not have a pH value of less than 5.30, the ester mixture surprisingly shows a synergistic effect and gives rise to pH values of around 4.73 under identical conditions.

Acidulant	Time (Minutes)																				
	0	10	15	20	25	30	35	40	45	50	55	60	65	70	75	80	85	90	95	100	
90% Triacetin/ 10% BDGE pH	8.55	8.24	8.01	7.90	7.71	7.62	7.52	7.40	7.28	7.12	6.93	6.61	6.23	5.93	5.73	5.65	5.56	5.51	5.47	5.43	
90% DBE/ 10% BDGE pH	8.70	8.34	8.19	8.02	7.88	7.76	7.64	7.51	7.37	7.21	7.00	6.71	6.39	6.09	5.78	5.65	5.55	5.44	5.34	5.30	
65% Triacetin/ 25% DBE/ 10% BDGE pH	8.65	8.02	7.77	7.69	7.53	7.47	7.35	7.21	7.06	6.90	6.55	6.20	5.71	5.34	5.10	4.96	4.84	4.77	4.73	4.73	

Claims

1. An acidulant for regulating the pH in textile processing characterised in that the acidulant comprises a mixture of triacetin and one or more esters of dibasic acids, said acidulant being substantially free of C_1-C_3 alkyl acetates.

2. An acidulant according to Claim 1 wherein the ester of dibasic acid used is selected from the C_1-C_4 alkyl esters of one or more saturated aliphatic dibasic acids having from 2 to 12 carbon atoms.

3. An acidulant according to Claim 1 or 2 wherein the ester used is an ester of a dibasic acid selected from oxalic, succinic glutaric and adipic acid and mixtures thereof.

4. A acidulant according to any one of the preceding Claims wherein the ester of dibasic acid used is a nylonate ester comprising in percentages by weight dimethyl succinate (15-25), dimethyl glutarate (55-65) and dimethyl adipate (12-23).

5. An acidulant according to any one of the preceding Claims wherein triacetin is present in an amount from 25-95%w/w of the total acidulant.

6. A process for regulating the pH during textile processing said process comprising using an acidulant according to any one of the preceding Claims wherein the pH is regulated by incorporating the acidulant during one or more of the following processing stages : scouring of the fabric, bleaching, chlorination, dyeing, mordanting, levelling, exhaustion, fixing, printing, finishing, water-proofing and milling.

7. A process according to Claim 6 wherein the acidulant is used to regulate the pH during the dyeing of wool.

8. A process according to Claim 6 or 7 wherein the concentration of acidulant used is in the range of 0.05-5%w/w based on the weight of the liquor being used in the dye bath.

9. An acidulant according to any one of the preceding Claims 1 to 6 wherein said acidulant is used to regulate the pH during textile processing to a value below 5.30.