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(54) Textile processing acidulants.

(57) This invention relates to the use of mixed esters comprising triacetin and n-alkyl acetates as acidulants during textile processing. The preferred alkyl acetate is n-propyl acetate. The acidulants are particularly suitable for use during dyeing of nylon fibres and fabric.

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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. A-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 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 thee 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 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 5.0-6.0) or (b) dyeing wool (pH 5.0-6.0). 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 an alkyl acetate.

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 esters triacetin and an alkyl acetate may be used as such or in combination with other esters such as glycol mono-and di-formates, glycol mono-and di-acetates, diacetin, diethyl oxalate or dialkyl succinates, or with free C_1-C_3 mono carboxylic acids. The alkyl acetate in the ester mixture is suitably an acetate ester of a C_1-C_5 monohydric alcohol, preferably a linear alcohol. n-Propyl acetate is most preferred. In the ester mixture comprising triacetin and the alkyl acetate, triacetin is suitably present in an amount from 25 to 95% w/w, preferably from 60 to 95% w/w of the total ester mixture.

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 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 0.1-10% 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 the the dying or printing process.

The type 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, prematallised, solvent, sulpher, vat dyes and optical brightners.

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

-pH control in the dying proces to achieve gradual change of pH from an alkaline 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 agents.

-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.

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:-

nPA - n-propyl acetate

Triacetin - glycerol triacetate

500 ml of distilled water was added to a 1 litre beaker contained in a water bath at 45°C. The water was allowed to equilibrate to 45°C and its pH adjusted to ca pH 9.0 using 25% ammonia solution (1 drop), 0.5g of the potential acidulant was then addd and the initial pH noted. The temperature of the solution was 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 30 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 5.86, the ester mixture surprisingly shows a synergistic effect and gives rise to pH values of around 5.3 under identical conditions.

Time (mins) / Acidulant	0	5	10	15	20	25	30	35	40	45	50	55	60	65	70	75	80	85	90	95	100
n-Propyl Acetate (nPA)* pH	8.87	8.81	8.78	8.74	8.71	8.65	8.59	8.41	8.23	8.09	7.76	7.63	7.56	7.48	7.39	7.25	7.12	7.04	6.93	6.80	6.67
Triacetin* pH	8.89	8.65	8.50	8.33	8.16	7.97	7.75	7.48	7.19	6.75	6.29	6.21	6.15	6.08	6.02	5.97	5.93	5.89	5.87	5.86	5.86
90% Triacetin/ 10% nPA pH	9.01	8.20	7.91	7.53	7.17	6.85	6.57	6.38	6.23	6.02	5.95	5.80	5.74	5.65	5.59	5.55	5.53	5.51	5.48	5.45	5.43
75% Triacetin/ 25% nPA pH	8.89	8.30	7.81	7.42	7.00	6.76	6.52	6.35	6.15	5.90	5.63	5.49	5.46	5.41	5.36	5.35	5.34	5.32	5.30	5.30	5.30
50% Triacetin/ 50% nPA pH	8.99	8.75	8.59	8.43	8.24	8.03	7.75	7.49	7.25	6.91	6.66	6.48	6.28	6.15	5.94	5.86	5.80	5.76	5.74	5.72	5.70

*Comparative Test not according to the invention

Claims

1. An acidulant for regulating pH in textile processing characterised in that the acidulant comprises a mixture of triacetin and an alkyl acetate.

2. An acidulant according to claim 1 wherein said acidulant contains in addition one or more of glycol mono-and di-formates, glycol mono-and di-acetates, diacetin, diethyloxalate, dialkyl succcinates and free C_1-C_3 monocarboxylic acids.

3. An acidulant according to claim 1 or 2 wherein the alkyl acetate in the mixutre is an acetate ester of a C_1-C_5 monohydric alcohol.

4. An acidulant according to any one of the preceding claims wherein the alkyl acetate in the mixture is n-propyl acetate.

5. An acidulant according to any one of the preceding claims wherein the mixture comprises from 25-95% w/w of triacetin.

6. An acidulant according to any one of the preceding claims wherein the acidulant is incorporated during textile processing at one or more of the stages selected from scouring of fabric, bleaching, chlorination, dyeing, mordanting, levelling, exhaustion, fixing, printing, finishing, water-proofing and milling.

7. An acidulant according to any one of the preceding claims wherein said acidulant is used for processing nylon fibre and/or fabric.

8. An acidulant according to any one of the preceding claims wherein the acidulant is used as a dye bath acidulant.

9. An acidulant according to claim 7 or 8 wherein said acidulant is used for pH regulation during winch dyeing of nylon apparels.

10. An acidulant according to claim 8 or 9 wherein the acidulant is present in a concentration of 0.1-10% w/w based on the weight of the liquor being used in the dye bath.