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RESEARCH ARTICLE

NOVEL ULTRA FILTRATION METHOD OF DIRECT BLACK 168, DYEING AND INK-JET PRINTING TO COTTON AND POLYAMIDE FIBRES

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ABSTRACT

The dye Direct Black 168 was purified using ultrafiltration technology and water based ink-jet inks were prepared for digital printing applications. The suitability of the inks for novel printing applications was evaluated via measurement of pH, conductivity, surface tension and viscosity over a period of 90 days. The inks were applied to cotton and polyamide fabric by digital printing. Also, dyeing with the dye before and after ultra filtration was done. Colour measurements and fastness properties were performed for the dyed and digitally printed samples. The results were promising and this paves the way for the production of environmentally friendly ink jet inks using pure direct dyes for the digital printing of cotton and polyamide through the formulation of suitable printing techniques.

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INTRODUCTION

Ultrafiltration technology is one of the newest technologies applied mainly for the treatment of textile effluents aiming at the desalination and the elimination of toxic pollutants in the discharged effluents (Maraicci *et al*., 2001; Ciardelli *et al*., 2001; Saffaj *et al*., 2004; Simonic, 2009; Kim *et al*., 2005). Ultrafiltration is the most modern ecological separation method acting as molecular separation method avoiding the use of chemicals. Typical UF membranes are synthetic organic polymers such as: poly (vinylidene fluoride), polysulphone, poly (ether sulphone), poly (acrylonitrile), poly (acrylonitrile)-poly (vinyl chloride) copolymers (Saeed *et al*., 2012). The use of ultrafiltration technology in dye synthesis allows the production of highly purified dyes with the elimination of inorganic salts either present in the raw materials or added during the synthesis process and also low molecular weight by products produced during the synthesis process (Simonic, 2009; Kim *et al*., 2005). The ultrafiltrated purified dyes have higher colouristic yield, brighter shades and higher solubility, thus allowing the production of high quality and high strength liquid formulations suitable for digital ink jet applications.

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The ultrafiltration technology has already been applied to an industrial scale for the production of pure liquid dyes for ink jet applications. Ink-jet printing is one of the fastest growing of imaging technologies; showing benefits over the conventional printing methods of roller and flat bed screen printing. These benefits include economic production of small runs, just in time delivery, quick response to fashion demands, no stock holding of chemicals and printed fabrics, no chemical waste, as well as low energy and water consumption (Fryberg, 2005; Daplyn *et al*., 2003; Holme, 2004). Commercially the first application of digital printing was for carpets (Dunkerley, 1981). This was launched in the 1970s and since then, developments over recent years have been dramatic (Dehghani *et al*., 2004; Tyler, 2005; Ujiie 2006). Presently, more than 30 billion square meters are printed per year resulting in a turnover of more than 140 billion Euros. Out of this 1.4 billion Euros is digitally printed (Fryberg, 2005). Conventional textile printing is predicted to grow at a rate of 2% per year, whereas digital textile printing is presently growing at a rate of 13%.and expected to reach a 20% growth rate in coming years (Provost, 1994; Stork Textile Printing Group, 2002; Cahill, 2004). Today the application areas of ink-jet printing cover the production of fashion apparel for men and women, sports and swimwear, home textiles such as curtains and sheets, automotive upholstery, flags and banners, T shirt, promotional material etc (Cahill, 2004). Water-based ink-jet inks offer environmental advantages over their non-aqueous based counterparts, through reduced emissions of volatile organic compounds that are otherwise present in solvent-based formulations. With environmental considerations continuing to have ever-greater impact upon industry and legislation, textile producers have to carefully examine the environmental impact of the products used. Water-based inks contain, typically, 30-80% water as a proportion of the total mass of the ink, together with a water miscible organic solvent such as a monohydric alcohol (methanol, ethanol, isopropanol), the colorant (e.g. disperse dye) and a surface active agent which, in the case of disperse dyes, acts as a dispersant for the dye in the aqueous medium (Kang, 1991; Yamamoto *et al*., 1997). The aim of this work was the purification by the use of membrane technology (ultrafiltration) of Direct Black 168 and the preparation of stable direct ink jet inks for digital printing applications. The inks were used for the digital ink jet printing of cotton and polyamide samples. The physicochemical properties pH, conductivity, surface tension and viscosity were studied over a period of 90 days. Also, conventional dyeing with Direct Black 168 before and after ultra filtration was applied to cotton and polyamide fibers. Fastness properties and colorimetric coordinates of the dyeings and prints were also performed. Finally, the dye before and after the Ultrafiltration was applied on cotton and polyamide fabric by exhaustion (dyeing).

MATERIALS AND METHODS

Commercially available lightweight (140 g/m^2) bleached knitted cotton fabric as well as nylon 6.6 (78F46, 1.69 dtexpf) supplied by KYKE HELLAS were used. Commercial sample of CI Direct Black 168 1 was kindly supplied by Yorkshire Colours; the dye was of press cake purity and contained no diluents (e.g. cutting agents, anti-dusting oil, dispersing agents) (Figure 1). 2-n-butoxyethanol from ALFA AESAR, Germany was used as the solvent for the inks preparation for ink-jet printing. Pretreatment auxiliary Penetral TBA was supplied by Prochimica, Italy. Digital printing auxiliaries for cotton and polyamide pretreatment, Kahafix R, used as antimigrating and fixing agent was supplied by KYKE HELLAS. Technical grade acetic acid and sodium acetate (CHEM-LAB), were also used.

Ultrafiltration

A laboratory ultrafiltration unit equipped with tubular membrane supplied by PCI Membranes (UK) was used throughout this work. The membrane used for the ultrafiltration process was the ES404, a polyethersulphone type membrane supplied by PCI Membranes (UK). Aqueous dye solution at 1.0% w/v Direct Black 168 was prepared at pH at 9 which was done with the addition of aqueous solution of 10% w/v NaOH. An initial volume of 1.5L of the dye solution was passed through the ultra filtration unit at constant temperature of 30-40 ^{0}C. Water of 3.0L at 40-50 ^{0}C was added into the unit to maintain initial volume of 3.0L constant keeping diafiltration rate at 1:2 volume. The flow rate was 51-66 $l/h/m^2$ and the unit was operating at approximately at 15 bar pressure constant for the whole duration. After the completion of diafiltration a concentration step was performed reducing the dye volume from 3.0:l to 1.0L.

Dyeing

Cotton and polyamide samples samples were pretreated using 2 g/l Penetral TBA, 1 g/l sodium carbonate at 80 C at liquor 1:25. Pretreated samples were then dried in open air. Dyeing was carried out in a Rotadyer dyeing machine (John Jeffreys Ltd, Rochdale Banbury, UK) with 2g fabric and depth of dyeing 0.25 0.5 1.0 1.5 2.0 4.0 6.0 8.0 10.0 % omf in a liquor ratio 1:25. Dyeing was performed for the cotton at 98^{o}C for 1h at pH 10 (5g/l Na_2CO_3 και 20 g/l NaCl, Figure 2a). For the polyamide the dyeing procedure was done at 98^{o}C for 1h and at pH 4 which was achieved with a buffer solution CH_3COOH-CH_3COONa (Figure 2b). The dyeing was done with the dye Direct Black 168 before and after ultra filtration.

Fastness properties

Wash fastness tests were carried out according to BS 1006 1990 CO6, C1S. Light fastness was determined according to BS 1006 1990 BO2 using a Q-SUN Xe-1-B xenon light fastness machine. Colour changes for all samples were assessed visually using a VeriVide D65 (UK) light cabinet (Standard Methods for the Determination of the Colour Fastness of Textiles and Leather, 1990).

Colour measurement

Colour measurements were performed using a Macbeth CE 3000 spectrophotometer under D65 illumination, 10^0 standard observer with UV included and specular component included. The samples were folded twice and four measurements were performed each time (MacDonald R (ed.), 1997).

The K/S values, were measured at the wavelength of maximum absorption using the equation 2:

$$K/S = \frac{(1-R)^2}{2R} \quad (2)$$

Where: K= absorbance coefficient
S= scattering coefficient
R= % reflectance

Ink formulation

The water-based ink formulations containing 1% w/v dye, 90% v/v H_2O and 10% 2-n-butoxyethanol as the water miscible solvent were prepared. The mixture of ingredients was stirred for 10 mins using an *Ultra Turrax T18 Basic* (IKA Inc.) homogenizer at 18000 rpm.

Cotton and polyamide pretreatment for digital printing

Cotton and polyamide samples were pretreated (80% pick up) in a solution containing Kahafix R 50 g/l (acting as an anti-migrating agent and fixing agent) and 5 g/l Acetic acid.

Surface tension, conductivity, viscosity and pH measurements

Surface tension measurements were made using a KSV Sigma 70 tensiometer (KSV Instruments, Helsinki, Finland) fitted with a Wilhelmy platinum ring. Conductivity measurements were performed using a Crison Conductimeter Basic 30 Crison, Barcelona, Spain) and pH measurements were made using a WTW Microprocessor 535 pH meter (Los Angeles, California, USA); viscosity measurements were made using a Viscostar plus+ H (Fungilab, Barcelona, Spain) viscometer. The above properties were measured at room temperature and atmospheric pressure for 1, 10, 20, 30, 60, 90 days.

Printing

Digital printing was performed on as above described pretreated cotton samples using an Epson Stylus SX218 ink-jet printer. After the digital printing the printed samples were dried at 120°C for 5 min.

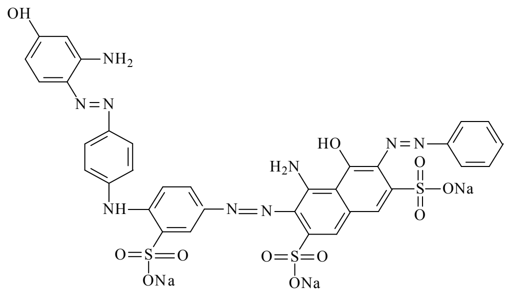

Figure 1. Structure of the dye Direct Black 168

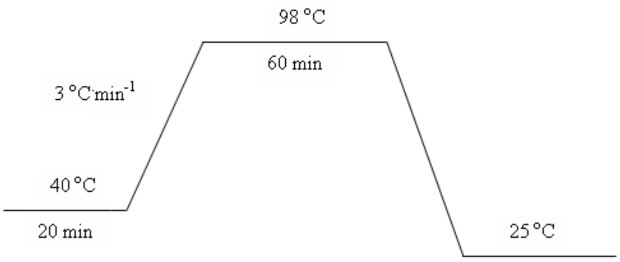

Figure 2(a-b). Dyeing process of: a. cotton b. polyamide fibre

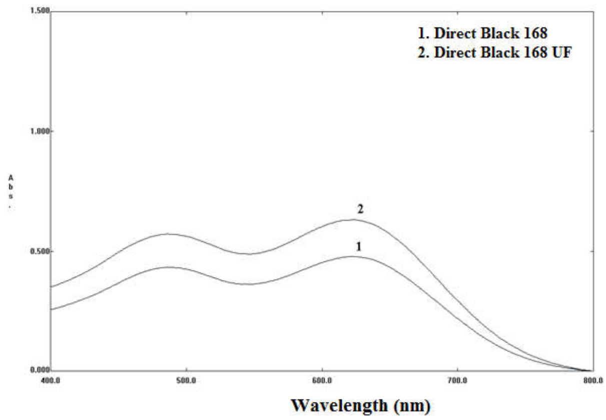

Figure 3. UV-Vis spectra of Direct Black 168 and Direct Black 168 UF

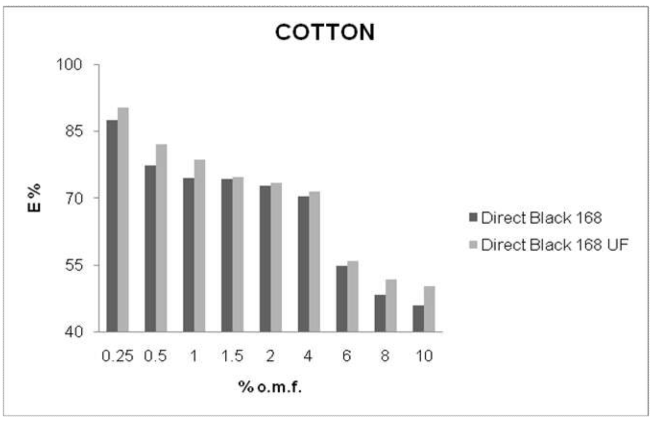

Figure 4. Exhaustion curves Direct Black 168 and Direct Black 168 UF on cotton fabric

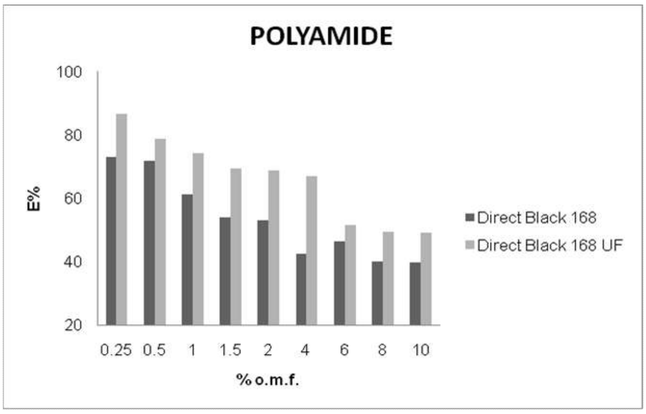

Figure 5. Exhaustion curves Direct Black 168 and Direct Black 168 UF on polyamide fabric

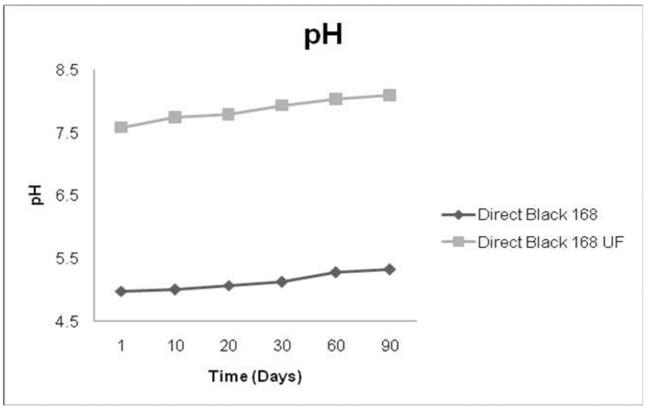

Figure 6. Plots of pH values vs time for the ink formulation

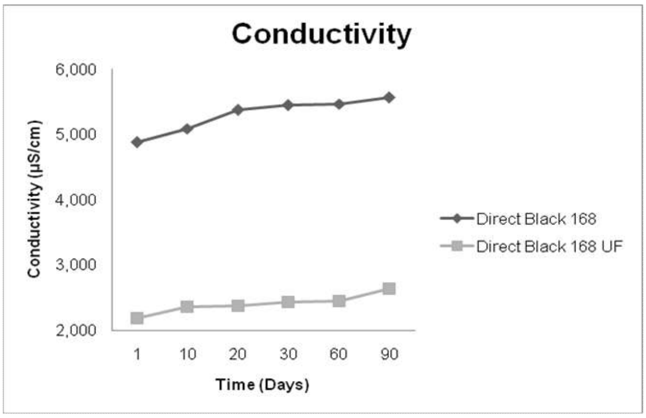

Figure 7. Plots of conductivity values vs time for the ink formulations

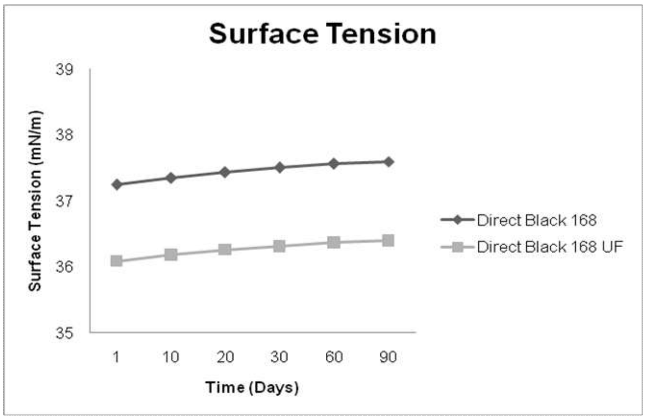

Figure 8. Plots of surface tension values vs time for the ink formulations

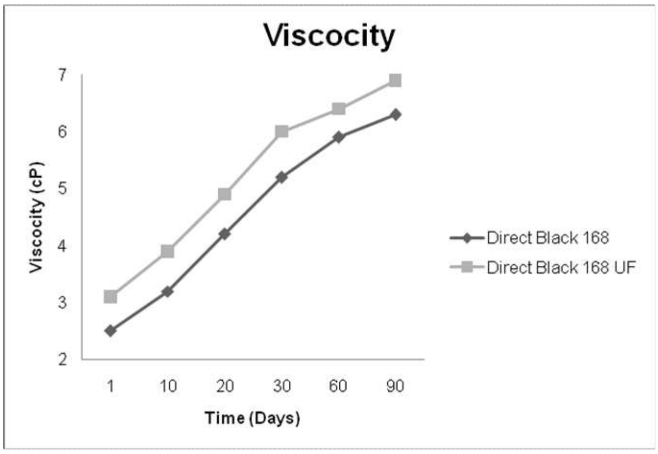

Figure 9. Plots of viscosity values vs time for the ink formulations

RESULTS AND DISCUSSION

Ultra filtration

The dye was passed through the ultra filtration unit housed with a PCI tubular ES404 polyamide membrane. Selection of UF membrane is of crucial importance. Membrane characteristics eg pore size, chemical nature, surface charge are critical in order to achieve selective separation with minimum dye loss. In Table 1 the % dye strength increase after ultra filtration is given. The elimination of all inorganic impurities results in the production of purer dyes as can be seen from the dye strength increase of the dyes after the ultra-filtration process which is 32.01% calculated from the absorbance at the corresponding λmax of the dyes before and after ultra filtration (Table 1). Ultra filtration also results in an improvement of the dye solubility, which is related with the dye crystallinity before and after ultra filtration.

Table 1. UV-Vis absorption before/after ultra filtration

	UV-Vis		% Dye strength
Dye	λmax	Abs.	Increase
Direct Black 168	621.5	0.478	32.01
Direct Black 168 UF	621.5	0.631	

Table 2. Colorimetric data L*,a*,b*,C, h^o and K/S values of the cotton and polyamide samples dyed with Direct Black 168 before and after ultra filtration

Dye o.m.f.	Fibre	K/S	λmax(nm)	L*	a*	b*	C	h^o
Direct Black 168, 0.25%	COTTON	3,40	640	44.59	-0.97	-7,12	7.19	262.20
Direct Black 168, 0.5%	COTTON	4,72	640	39.76	-0.20	-7.06	7.07	268.34
Direct Black 168, 1.0 %	COTTON	5,63	630	34.45	1.17	-4.84	4.98	283.59
Direct Black 168, 1.5%	COTTON	6,98	610	30.46	1.47	-4.03	4.29	290.02
Direct Black 168, 2.0 %	COTTON	8,72	500	29.00	2.00	-3.27	2.84	301.48
Direct Black 168, 4.0 %	COTTON	12,72	500	24.83	1.95	-2.71	3.34	305.73
Direct Black 168, 6.0 %	COTTON	17,39	510	20.79	0.74	-3.70	3.74	281.60
Direct Black 168, 8.0 %	COTTON	19,59	490	16.78	0.54	-2.98	2.97	280.72
Direct Black 168, 10.0 %	COTTON	21,04	500	16.61	0.57	-2.88	2.94	281.25
Direct Black 168, 0.25%	PA	2,64	640	48.80	-2.60	-5.71	6.27	245.54
Direct Black 168, 0.5%	PA	4,49	640	42.29	-2.50	-6.21	6.69	248.06
Direct Black 168, 1.0 %	PA	8,74	640	32.64	-2.80	-5.89	6.52	244.59
Direct Black 168, 1.5%	PA	10,84	640	29.28	-2.73	-5.61	6.24	244.06
Direct Black 168, 2.0 %	PA	13,81	640	26.47	-2.57	-5.32	5.95	243.69
Direct Black 168, 4.0 %	PA	17,39	640	23.05	-2.22	-3.77	4.38	239.52
Direct Black 168, 6.0 %	PA	21,34	640	18.11	-1.47	-3.64	3.93	248.05
Direct Black 168, 8.0 %	PA	26,04	640	16.49	-1.34	-3.60	3.84	249.55
Direct Black 168, 10.0 %	PA	28,95	640	16.35	-1.36	-3.46	3.70	247.95
Direct Black 168, 0.25%	COTTON	3,67	640	43.69	-1.33	-6.76	6.89	258.86
Direct Black 168, 0.5%	COTTON	5,42	640	37.35	-0.39	-6.64	6.65	266.60
Direct Black 168, 1.0 %	COTTON	8,34	630	30.91	0.38	-5.38	5.40	274.05
Direct Black 168, 1.5%	COTTON	9,23	630	28.24	0.73	-4.59	4.64	279.05
Direct Black 168, 2.0 %	COTTON	11,22	500	23.86	1.13	-3.53	3.74	289.45
Direct Black 168, 4.0 %	COTTON	16,32	500	19.90	1.14	-2.64	2.87	293.43
Direct Black 168, 6.0 %	COTTON	18,24	510	19.96	1.04	-2.28	2.50	294.82
Direct Black 168, 8.0 %	COTTON	22,05	500	18.98	1.09	-2.44	2.67	294.05
Direct Black 168, 10.0 %	COTTON	25,61	510	17.24	0.87	-2.07	2.25	292.86
Direct Black 168, 0.25%	PA	2,76	640	48.72	-2.54	-5.49	6.05	245.13
Direct Black 168, 0.5%	PA	5,27	640	38.94	-2.82	-5.98	6.61	244.73
Direct Black 168, 1.0 %	PA	11,31	640	30.06	-2.63	-569	6.27	245.17
Direct Black 168, 1.5%	PA	13,81	640	26.47	-2.57	-5.32	5.95	243.69
Direct Black 168, 2.0 %	PA	18,25	640	22.92	-2.27	-5.00	5.49	245.57
Direct Black 168, 4.0 %	PA	20,75	640	21.70	-2.04	-4.43	4.88	245.22
Direct Black 168, 6.0 %	PA	25,05	640	17.76	-1.45	-3.44	3.74	247.22
Direct Black 168, 8.0 %	PA	28,77	640	18.42	-1.40	-3.13	3.43	245.88
Direct Black 168, 10.0 %	PA	30,66	640	17.88	-1.51	-3.15	3.50	244.40

Table 3. Colorimetric data L*,a*,b*,C, h^o and K/S values of the cotton and polyamide samples printed with Direct Black 168 before and after ultra filtration

Dye	Fibre	K/S	λmax(nm)	L*	a*	b*	C	h^o
Direct Black 168	COTTON	1,35	630	54.00	-0.44	-1.69	1.75	255.31
Direct Black 168	PA	0,31	630	70.90	0.04	0.33	0.33	271.44
Direct Black 168UF	COTTON	1,53	630	54.59	-0.46	-3.02	2.98	261.27
Direct Black 168UF	PA	0,86	630	62.67	0.04	-1.72	1.72	282.46

The dye strength increase (Table 1) coupled with the dye solubility increase clearly shows that the ultra filtration has dramatically improved the quality of the dyes. The dye quality improvement resulted by this membrane technology opens new areas of application of the ultra filtrated dyes such as in ink jet digital printing where dye purity and solution stability is of paramount importance. In Figure 3 the UV-Vis spectra of the Direct Black 168 and Direct Black 168 UF respectively are given.

Dyeing

Aqueous solutions of the dye and the same dye after ultra filtration were used for the dyeing of cotton and polyamide fibres (Figures 4,5). Figures 4, 5 show the exhaustion values at 0.25, 0.5, 1.0, 1.5, 2.0, 4.0, 6.0, 8.0 and 10.0 % o.m.f. Direct Black 168 and Direct Black 168 UF at 98^{o}C respectively in cotton and polyamide samples. The exhaustion values are higher on cotton than polyamide and this can be attributed to the fact that Direct Black 168 is a large molecular weight dye showing high substanbility to cotton due to its large molecular size promoting the formation of van der Waals forces between the dye and the fibre. The exhaustion values of all dyed samples with ultra filtrated dye are higher than the corresponding values obtained with non ultra filtrated dyed samples in all cases. This can be attributed to the removal of inorganic salts and other impurities in the permeate solution, resulting a much purer dye.

Ink-jet printing

Ink-jet ink formulations were prepared using the dye before and after ultrafiltration. The elimination of inorganic salt impurities, the increased coloristic yield coupled with the higher solubility of the ultrafiltrated dye make the ultrafiltrated dye extremely suitable for the production of high quality digital printing inks avoiding nozzle damages and blockages. Monitoring a digital ink formulation over a period of time is a widely accepted method for evaluating stability of the ink jet ink (Daplyn *et al*., 2003; Kang, 1991). In this study the pH, conductivity, surface tension and viscosity of the ink jet ink formulations prepared with direct dyes were monitored over a period of 90 days. In Figure 6 the plots of the pH values against time are given for the inks. The pH stability of the ink jet inks remains relatively stable over the period of 90 days which is a good indication regarding the suitability of the inks for digital printing application. From above figures it can be concluded that the formulation with the dye Direct Black 168 has lower pH than the other ink. This is due to the fact that the dye has been milled and processed in lower pH. The inks with the dye Direct Black 168 UF have higher values of pH because the ultra filtration procedure was done at pH 9. According to the literature commercial ink jet ink formulations should have pH values near the neutral region (Daplyn *et al*., 2003; Holme, 2004; Kang, 1991). No adjustments were of pH were made for the ink jet inks prepared. However the pH of Direct Black 168 needs a slight correction because it is in acid region.

Figure 7 shows the conductivity values of the two digital printing inks over a period of time 90 days. Ink jet ink with Direct Black 168 UF show lower conductivity values than the Direct Black 168 which can be attributed to the elimination of all inorganic impurities. The conductivity in both cases increases due to the complete ionization of the sulphonic acid groups in the dye molecules during the time. Surface tension (Figure 8) of the two prepared direct inks is within acceptable limits 21-48mN/m for digital printing application remaining relatively constant over a period of 90 days (Daplyn *et al*., 2003; Holme, 2004; Kang, 1991). As can be seen the surface tension of all inks prepared remains relatively constant after an intitial slight increase up to 30 days storage time. All inks prepared have surface tension values within the proposed ranges. The stability of the surface tension over a period of 90 days shows that all inks prepared are suitable to be used as ink-jet inks. The ultrafiltration does not adversely affect the surface tension and despite a slight decrease surface tension values lie within the acceptable limits. This slight decrease in surface tension can be attributed to the elimination of all inorganic impurities which results in the production of purer dyes. Surface tension increase is at the benefit of the adhesional wetting of the ink. Figure 9 show the effect of storage time on viscosity. It is generally accepted that ink jet inks should have a viscosity lower than 2cP to be suitable for digital printing application although it is not unknown for such inks to have a viscosity up to 3cP (Siemensmeyer, 1993). Both Direct Black 168 and Direct Black 168UF inks showed an intitial sharp increase in viscosity after 10 days of storage. This temporary increase in viscosity can be attributed to the sulphonic acid groups in the dye molecules which produce more anionic repulsions and thus causing a increment in viscosity during time (Siemensmeyer, 1993).

Colorimetry

The colorimetric values of the dyed samples are given in Table 2. The K/S values of all dyed samples with ultra filtrated Direct Black 168 are higher than the corresponding K/S values obtained with non ultra filtrated Direct Black 168. The colour strength obtained for the dyeing with the Direct Black 168 and Direct Black 168 after ultrafiltartion is higher as can be exemplified by the higher K/S and the lower L values obtained for the ultrafiltated dyes on both cotton and polyamide application. The increase in dye uptake obtained for the ultrafiltrated dyes compared to the non ultrafiltrated ones shows again that the ultrafiltration process resulted in dyes with higher coloristic yield. This is in agreement with previous findings (Table 1) shown the % dye strength increases measured from the dye solutions before and after ultra filtration and can be explained in same terms as above with the removal of inorganic salts and other impurities in the permeate solution. The other colouristic co-ordinates such as L, a, b, C, h^o values are in line with strength changes not showing significant colour changes before and after ultra filtration. The inks prepared were used to print cotton and polyamide samples which were pretreated as described above. In Table 3 colorimetric data L*,a*,b*,C, h^o and K/S values of the prints are given. Compared to the dyeing, the K/S values of the cotton prints were in all cases significantly low (Tables 2, 3). This can be attributed to the low quantity of the colorant, sometimes insufficient, reaching the surface of the sample (droplets through the fine nozzles at high speed) and the possible low dye solution concentration employed for the preparation of digital printing inks. The printed samples with Direct Black 168 UF have higher K/S values than the non ultrafiltrated dye as was also the case with the dyed samples. The colorimetric values from Table 3 also show that ultrafiltration results not only in a more concentrated dye, as this can be shown from the much higher K/S values,on both cotton and polyamide, but also in a in a much purer bluer dye as this can be seen from the lower b values and the higher C values.

Table 4. Wash and light fastness of cotton and polyamide samples dyed with Direct Black 168 before and after ultra filtration

Dye o.m.f.	Fibre	Wash fastness		Light fastness
		*CC	*CS	
Direct Black 168, 0.25%	COTTON	4/5 -5	DIAC=5,COT=4,PA=5,PES=5,PAC=5,W=5	3
Direct Black 168, 1.0%	COTTON	4/5 -5	DIAC=5,COT=3,5,PA=5,PES=5,PAC=5,W=5	3-4
Direct Black 168, 2.0%	COTTON	4/5 -5	DIAC=5,COT=3,PA=5,PES=5,PAC=5,W=5	4-5
Direct Black 168, 0.25%	PA	4- 5	DIAC=5,COT=4,5,PA=5,PES=5,PAC=5,W=5	3
Direct Black 168, 1.0%	PA	4- 5	DIAC=5,COT=4,5,PA=5,PES=5,PAC=5,W=5	3
Direct Black 168, 2.0%	PA	4- 5	DIAC=5,COT=4,5,PA=5,PES=5,PAC=5,W=5	3-4
Direct Black 168, 0.25%	COTTON	5	DIAC=5,COT=4,5,PA=5,PES=5,PAC=5,W=5	3
Direct Black 168, 1.0%	COTTON	4/5- 5	DIAC=5,COT=4,PA=5,PES=5,PAC=5,W=5	4
Direct Black 168, 2.0%	COTTON	4/5 -5	DIAC=5,COT=3,5,PA=5,PES=5,PAC=5,W=5	4-5
Direct Black 168, 0.25%	PA	5	DIAC=5,COT=4,5,PA=5,PES=5,PAC=5,W=5	4-5
Direct Black 168, 1.0%	PA	5	DIAC=5,COT=5,PA=5,PES=5,PAC=5,W=5	4-5
Direct Black 168, 2.0%	PA	5	DIAC=5,COT=5,PA=5,PES=5,PAC=5,W=5	5

*CC=Color Change, *CS=Color Staining, DIAC=Diacetate, COT=Cotton, PA=Polyamide, PES=Polyester, W=Wool

Table 5. Wash and light fastness of cotton and polyamide samples printed with Direct Black 168 before and after ultra filtration

Dye	Fibre	Wash fastness		Light fastness
		*CC	*CS	
Direct Black 168, 0.25%omf	COTTON	3/4 -4	DIAC=5,COT=3,PA=5,PES=5,PAC=5,W=5	2-3
Direct Black 168, 0.25%omf	PA	2/3 -3	DIAC=5,COT=2,5,PA=5,PES=5,PAC=5,W=5	4
Direct Black 168 UF, 0.25%omf	COTTON	3/4 -4	DIAC=5,COT=3,PA=5,PES=5,PAC=5,W=5	3
Direct Black 168 UF, 0.25%omf	PA	2/3 -3	DIAC=5,COT=2,5,PA=5,PES=5,PAC=5,W=5	4-5

*CC=Color Change, *CS=Color Staining, DIAC=Diacetate, COT=Cotton, PA=Polyamide, PES=Polyester, W=Wool

This can be explained in terms that the ultrafiltrated dye has much less dulling imporities which were removed during the UF process. The localised digital printing application of the ink drops of the dye make this more moticable in the digital printing rather than in the dyeing process.

Wash and light fastness

The fastness data obtained for the dyed samples before and after ultra filtration are given in Table 4. The staining of the wool, polyester, acetate, nylon and acrylic fibres in the multifibre strip were found to be 5 in all cases. As it was expected the cotton was stained more by Direct Black 168 which is a large molecular weight cotton dye.. The color change was in all cases from very good to excellent. Light fastness were medium to low. Ultra filtration slightly improves the fastness properties of the dyed samples. The multifibre staining of the washed samples for printed samples, was worse on cotton and excellent on the other fibres (Table 5). The staining behavior resembles the one of common direct dyes on cotton. Light fastness is also medium to low. The fastness properties of the printed samples using the ultrafiltrated dye were slightly improved because of the ultra filtration.

Conclusion

The dye Direct Black 168 was ultrafiltrated with using ES404, a polyethersulphone type membrane. The ultrafiltration resulted in the production of purer dye this can be seen from the dye strength increase of the dyes after the ultra-filtration process. Ultrafiltrated digital ink jet printing inks were prepared and their properties such as pH, conductivity, surface tension, viscosity were monitored over a period of time. The ultra filtrated and the non ultra filtrated counter parts were used to dye and print digitally cotton and polyamide samples. The exhaustion values were higher on cotton than polyamide. The exhaustion values of all dyed samples with ultra filtrated dye are higher. The removal of inorganic salts and other impurities in the permeate solution, results in a much purer dye. Fastness properties and colour measurements were performed for the dyed and digitally printed samples. Both dyed and printed samples had medium to low wash and light fastness. Ultra filtration slightly improves the fastness properties of the dyed samples. Colouristic values of the dyed/ printed samples were as it was expected, i.e. K/S values of the dyed samples were higher than printed ones. K/S values of the dyed samples with the ultra filtrated dye were higher than those with the initial dye and the rest colouristic co-ordinates L*,a*,b*,C, h^o were in line with strength changes of the dye before and after ultra filtration and in the case of digitally printed samples show that not only stronger but much brighter and cleaner ink jet due ink formulations were produced. The implementation of ultra filtration process in Direct Black 168 allowed the production of purer and cleaner dyes with increased colouristic yield and the production of stable water based digital printing inks. Ultra filtration technology opens new areas of dye applications in the high added value of digital printing industry. The results were promising and this paves the way for the production of environmentally friendly ink jet inks using pure dyes for the digital printing of cotton and polyamide through the formulation of suitable printing techniques.

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