Asian Journal of Chemistry Vol. 21, No. 6 (2009), 4871-4880

Synthesis and Characterization of Styrene-Acrylic Binders and Their Application on Pigment Printing of Cotton and Polyester Textile Fabrics

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This paper reports the synthesis and characterization of styrene-acrylic binders. 2-Ethylhexylacrylate styrene (2-EHA), ethyl acrylate styrene (EA), methyl methaacrylate styrene (MMA), butyl acrylate styrene (BA) copolymers were prepared by emulsion copolymerization. The polymerization was performed with methaacrylic acid (MAA) and auxiliary agents at 80 ºC in the presence of ammonium persulphate (APS) as the initiator. Sodium lauryl ether sulphate was used as non-ionic emulsifier. The resulting copolymers were characterized by Fourier transform infrared spectroscopy (FTIR) and then effect of initiator on the properties of the styrene-acrylic binders emulsion copolymers were discussed. A printing paste comprising synthetic thickener, emulgator, styrene-acrylic binders, Imperon brilliant red B was applied using a flat screen printing technique on to the cotton and polyester fabrics, then dried and exposed to heat in different temperature. The characteristics of cured prints such as paste add-on, colour fastness to washing and dry/wet rubbing were evaluated, together with fabrics stiffness. types of textile fabrics using pigment dyes.The highest K/S is obtained and the fastness properties range between good and excellent for samples printed using methyl methaacrylate styrene (MMA) based, this is true irrespective of the type of printed fabric. The lowest K/S is obtained in case of using ethyl acrylate styrene (EA) as a commercial binder. The binder of 2-ethylhexylacrylate (2-EHA) gives K/S better than the binder of butyl acrylate styrene (BA) for two types of printed fabrics.

Key Words: Styrene-acrylic binders, Pigment printing of cotton, Polyester textile fabrics.

INTRODUCTION

Pigment textile printing is not only the oldest process, but also more than 80 % of the printed goods are based on pigment printing to its obvious advantages, such as versatility, ease of near final print at the printing stage itself[1], *etc.* This pigment printing makes use of mineral turpentine which is involved in making emulsion

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thickeners. This pigment printing makes use of mineral turpentine which is involved in making emulsion thickeners. In this system, the oil in the emulsion gets evaporated to the atmosphere at the time of curing of the pigment printed fabric[2-4]. It is almost impossible to reclaim this kerosene. In spite of the superior thickening properties of oil/water emulsion which also contribute towards a soft hand of the print, good fastness properties, ease of application methods and economy and several other factors have compelled the search for a replacement for oil.

The use of synthetic thickening agents and new developments in printing auxiliaries have also contributed to the increasing importance of pigment printing. During pigment printing process, the environmental aspects such as minimization of formaldehyde emissions and carbon dioxide content must be taken into account[5]. At the same time, novel binder systems allow a much softer handle to be attained[5]. Formaldehyde emissions and clogging on the screens during the actual printing process must also be taken into account. These disadvantages are related to the binders used[6-8].

The aim of this work was to examine some novel synthesis aqueous binders having normal viscosity and the new idea is not only fixation of the pigment dye through the polymerization process of the binder but also printing all types of fabrics using pigment dyes[9,10].

EXPERIMENTAL

Imperon brilliant red B, methyl methaacrylate (Fluka), butyl acrylate, 2-ethyl hexyl acrylate and ethyl acrylate, N-methylol acryl amide, acrylic acid, styrene, ammonium persulphate (Merck), ammonia (Merck) and sodium lauryl ether sulphate (Henkel, Germany)[11]. Aqueous binders of methaacrylic acid (MMA) based on either butyl acrylate (BA), ethyl acrylate (EA) and 2-ethyl hexylacrylate (2-EHA) had been synthesized. Acraconz BN (thickener synthetic) Bayer Co, Germany. Ammonium sulfate $(NH_4)_2SO_4$, Merck, Germany. Desizing, scoured, bleached and mercerized wave cotton fabric (100 % cotton 130 g/m^2) and polyester fabric (100 % PES 90 g/m^2) supplied by TexlabCo. Urea MERCK, Germany. Emulsifier V02 Bayer Co, Germany[10-12].

Polymerization procedure: Semi-continuous emulsion copolymerization were carried out using a 500 mL five necked round-bottom flask equipped with a reflux condenser, stainless-steel stirrer device and two separate feed streams. The first feed stream was a solution of MMA, BA, EA and 2-EHA and anionic surfactant. The other feed was the initiator solution before emulsion polymerization start up, the reaction vessel was first charged with the desired amounts of water, emulsifier and initiator solution, respectively. During polymerization, the reaction mixture was stirred at a rate of 60 rpm and the temperature was maintained at 60 ºC.

After 5 min, a 10 % of total amount of the monomer mixture was added to the flask in a period of 20 min. Then the temperature was kept at 80 ºC until the end of polymerization. The polymerization was performed with feeding rate of 1.0 mL/

min. The reaction was cooled to room temperature and neutralized, if necessary, to a final pH of 8. The binders were then filtered through 100-mesh and 325-mesh screen. The copolymerization and analyzing of the binders is shown in Tables 1 and 2.

TABLE-1
POLYMERIZATION RECIPES AT 800C

Compound	Binder MMA (%)	Binder BA (%)	Binder EA (%)	Binder 2-EHA (%)
Water	58.85	58.85	58.85	58.85
Butyl acrylate	–	19.00	–	–
Ethyl acrylate	–	–	19.00	–
Methyl methaacrylate	19.00	–	–	–
2-EHA	–	–	–	19.00
Styrene	15.00	15.00	15.00	15.00
Acrylic acid	1.50	1.50	1.50	1.50
NMA	2.50	2.50	2.50	2.50
SLES	1.80	1.80	1.80	1.80
Ammonia	1.10	1.10	1.10	1.10
Ammonium per sulphate	0.25	0.25	0.25	0.25

NMA = N-Methylol acryl amide, SLES = Sodium lauryl ether sulphate.

TABLE-2
DIFFERENT TESTING AND ANALYZING RESULTS OF ON THE BINDERS

Binders	MFFT (ºC)	pH	Tg (ºC)	Solids (%)
2-EHA	<-5.0	7.8	-5.0	48
BA	<-4.0	7.8	-4.8	50
EA	<-3.7	7.8	-3.5	49
MMA	<-3.0	7.8	-3.0	51

Printing recipe: The pigment printing pastes were prepared according to the following recipe: imperon (pigment) dye (3-5 %), acraconz BN (1-1.5 %), binder (3-5 %), ammonium sulfate (2 %), urea (0.5 %), acramine softener MPG (1.5-2.0 %), distilled water[2,3] (balance to 100 %).

Printing technique: The fabrics printing was carried out using screen printing machine, type VP-AL-500, Germany, the printed fabrics were dried in at 95-100 ºC, the goods were subjected to thermal treatment in a thermostatic oven (Mathis, Switzerland) to fixation at 150 ºC the colour through the polymerization process. After that the printed goods were subjected to washing 45 ºC with 1 g/L soap (Diadavin EWN Bayer C0, Germany) rinsing thoroughly with cold water.

Testing and analysis

Rheological properties: The rheological propertes and apparent viscosity of the printing pastes were measured using fluids spectrometer RFS II (Rheometrics CO 1483), Germany at 250C and at different shear rates.

Colour measurements: The relative colour strength of the prints, expressed as K/S value[12] of the printed samples was determined by reflection measurements using data colour international model SF 500, USA.

Fastness properties: Fastness to washing, rubbing[9] and perspiration was assessed according to the standard (AATCC) methods[11].

RESULTS AND DISCUSSION

Solubility and FTIR analysis: The emulsion copolymers basically have low solubility or do not have any solubility in organic solvents at all. These copolymers, which have been synthesized from 2-EHA with or without NMA, are not exceptions. They are not soluble even in aprotic polar solvents such as NMP, DMSO and DMF. This insolubility could be due to conversion of the polymer samples to gelation immediately during of drying under air atmosphere or vacuum. Different procedures for the preparation, purification and drying of the polymer samples were carried out. For example, the product was isolated by filtration after precipitation with a large amount of methanol and dried under vacuum at 60 ºC. After 48 h it was observed that it is insoluble in all of the above-mentioned solvents. It is worth to mention that the obtained copolymers will turn to gel by adding 2 drops of ethanol after dissolving in the DMF, DMSO, THF, toluene and benzene, respectively. The characterization of these copolymers is difficult due to their insolubility behaviour. FTIR spectra in the region from 4000 to 500 cm^{-1} were recorded with a sample prepared by making a film of the latex on the surface of a glass and drying it, then removing the film from the glass. Fig. 1 shows the FTIR spectra of (A) 2-EHA and (B) with 0.25 mol L^{-1} NMA added copolymers, respectively. The comparison of spectra with B has not shown any differences between two different samples of copolymers. The same analyses were repeated for each sample 3 times and from the FTIR data it was concluded that this method is not able to show the presence of NMA moiety in these kinds of copolymers.

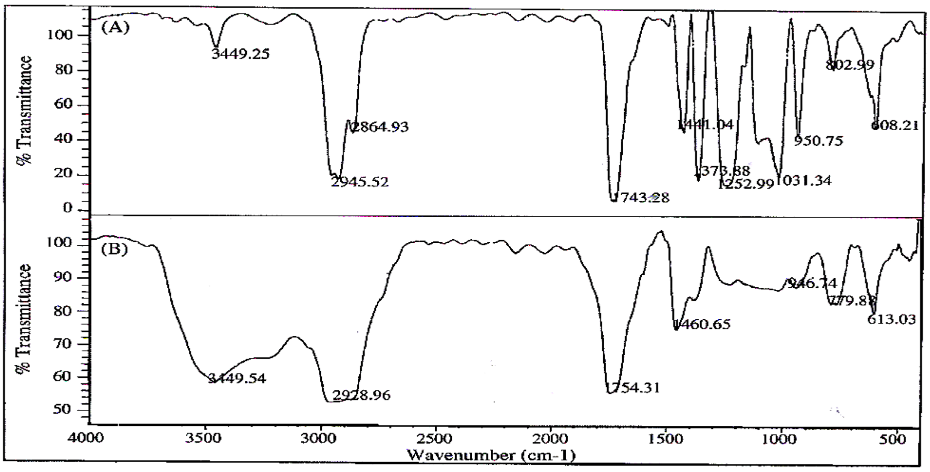

Fig. 1. FTIR spectra of (A) 2-EHA copolymer and (B) with 0.25 molar NMA. [M]0 = 5.30 mol L^{-1}, 60 rpm, [I]0 = 8.40×10^{-3} mol L^{-1}, T = 80 ºC

Effect of initiator concentration: Fig. 2 shows the variation of conversion with time at three initiator levels. As is expected, polymerization rate increases with increasing initiator concentration. This behaviour can be explained as follows. First, the higher the initiator concentration, the higher the number of adsorbed fixed radicals on the particle surface and therefore the lower the retardation of polymerization due to the seed particles.

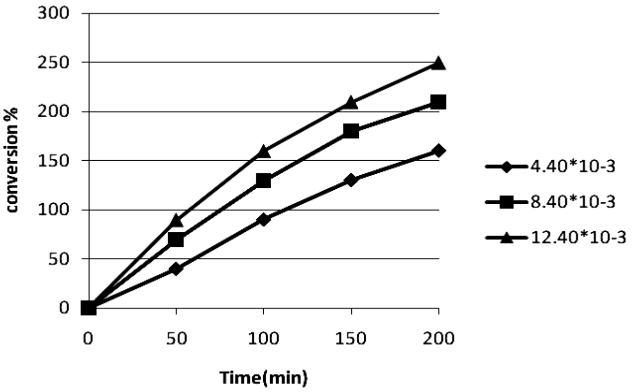

Fig. 2. Effect of initial initiator concentration on monomer conversion time at $[(NH_4)_2.S_2O_8] \times 10^{-3}$, 60 rpm T = 80 ºC

Secondly, with increasing initiator concentrations the proportion of usual emulsion polymerization increases in the aqueous phase and at high initiator concentrations, the proportion of surface layer polymerization will be negligible. This difference may also be attributed to the homogeneous nucleation of particles that is typical in vinyl acetate emulsion polymerization. Analyzing the above results, it is difficult to decide what is the main effect.

Rheological properties of freshly prepared printing paste: This work was carried out with the following three main objectives *i.e.*, elimination of either oil/ water emulsion or formaldehyde emissions in pigment printing by using some novel prepared binder containing unsaturation sites which is responsible for fixation of the pigment through polymerization process.

Printing of all types of fabrics using the pigment dye, through this technique, which is dependent on the fixation of the dye through the polymerization process that happened to the binder used under the effect of the temperature of fixation.

Since the rheological properties of the printing pastes and their viscosity are responsible for controlling dye penetration, depth of shade, sharpness of the print and levelness, it is of great interest to investigate the rheological properties of the printing pastes.

The rheological properties and apparent viscosity of freshly prepared printing pastes using 1.0-1.5 % acraconz BN and 40 % of styrene acrylate based on EA using 3 and/or 5 % imperon brilliant red B are shown in Figs. 1 and 2, respectively.

It is clear from Figs. 1 and 2 that all the samples examined were characterized by non-Newtonian pseudo plastic behaviour, where the up and down flow curves are coincident. It is also clear from Figs. 3 and 4 that the location of the rheogram and its slope seems to be dependent not only on the type of binder used but also on the concentration of dye used, which indicates.

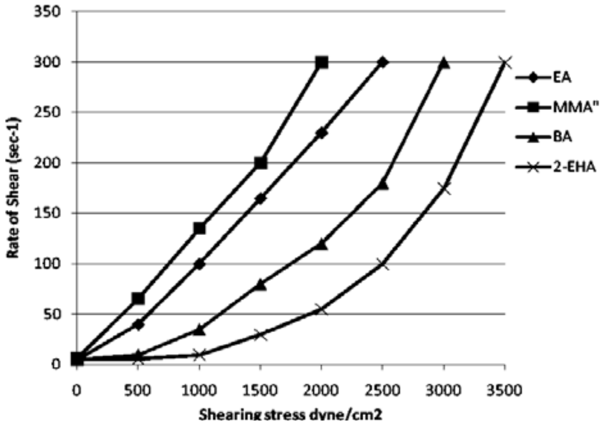

Fig. 3. Rheological properties of freshly prepared printing pastes using 1-1.5 % acraconz BN and 40 % of synthetic binder of styrene acrylate based on using 3 % imperon brilliant red B

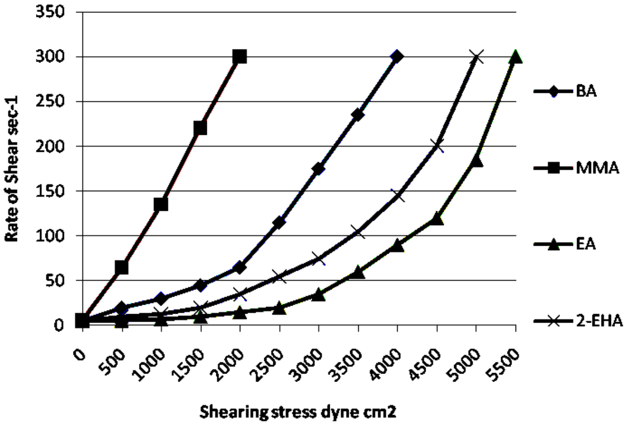

Fig. 4. Rheological properties of freshly prepared printing pastes using 1-1.5 % acraconz BN and 40 % of synthetic binder of styrene acrylate based on using 5 % imperon brilliant red B

A variation in the apparent viscosity the rheogram curve of the commercial binder used (EA containing 3 % dye) was shifted nearest to the axis of the rate of shear indicating a decrease in its apparent viscosity as shown in Fig. 3, while on using 5 % dye, the rheogram curve was shifted far from the axis of the rate of shear indicating an increase in its apparent viscosity.

As shown in Fig. 4, at a rate of shear 10.0007s1, the apparent viscosity of EA increased from 2.19 to 5.303 Pas, while it decreased from 6.348, 4.757 and 1.593 to 3.984, 3.425 and 1.327 Pas in case of using BA, based on respectively, by increasing the amount of dye used from 3 to 5 %. This may be due to the difference in the chemical constituent of prepared binder and the commercial binder used, may be the dispersant medium of the pigment dye containing some groups which make cross-links or form hydrogen bonding with the EA which lead to an increase in its molecular weight and leads to increase in its viscosity.

Screen printed cotton and polyester fabrics: The effect of increasing the fixation temperature on the colour strength of screen printing on either cotton or polyester upon using EAS as a commercial binder and BAS containing imperon brilliant red B of different concentrations 3 and 5 % and the time of fixation of 2 min are represented in Figs. 5-8, respectively. It is clear from the Figs. 5-8 that the colour strength of the printed fabrics (using either 3 % or 5 % dye) is nearly comparable. This may be attributed to the increase in the dye concentration needed to increase in the binder concentration to make fixation to this dye through the polymerization process to this binder.

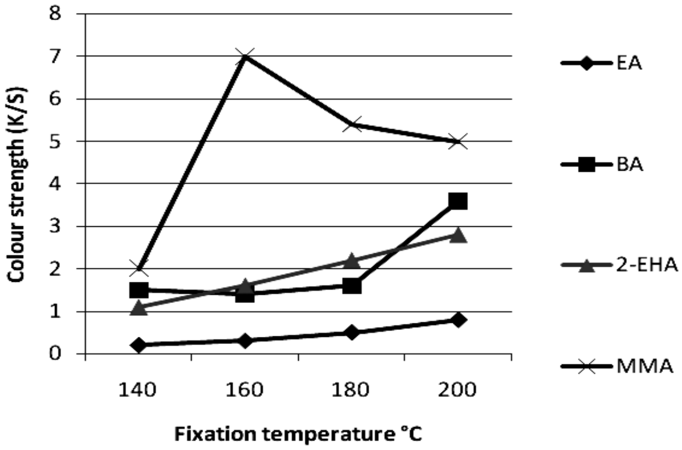

Fig. 5. Effect of the type of binders used on the colour strength of screen printed cotton fabrics using 3 % imperon brilliant red B, the time of fixation is 2 min

It is also clear from Figs. 5-8 that the highest colour strength values were obtained in case of using styrene acrylate based as a binder in the printing paste as compared to the results obtained upon using the commercial binder of EA, which gives the lowest value of colour strength in case of screen printed cotton fabrics, while in case of using 2-EHA, the K/S values were better than the values obtained in case of using BA. For example, the K/S values of screen printed cotton and polyester fabrics fixed at temperature 160 ºC were 0.31, 1.9, 1.77, 6.83 and 0.85, 1.01, 0.65, 4.73 by using E, styrene based on 2-EHA, styrene based on BA, styrene

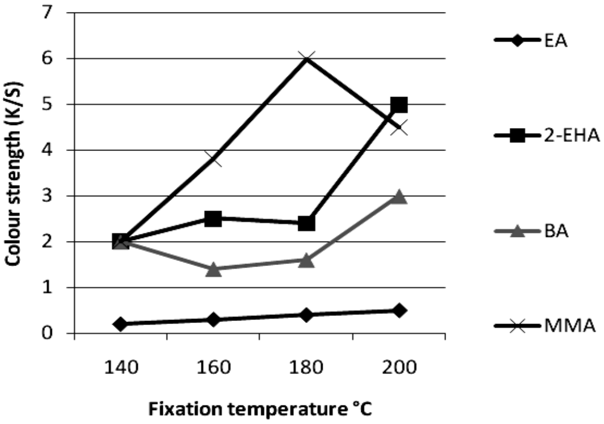

Fig. 6. Effect of the type of binders used on the colour strength of screen printed cotton fabrics using 5 % imperon brilliant red B, the time of fixation is 2 min

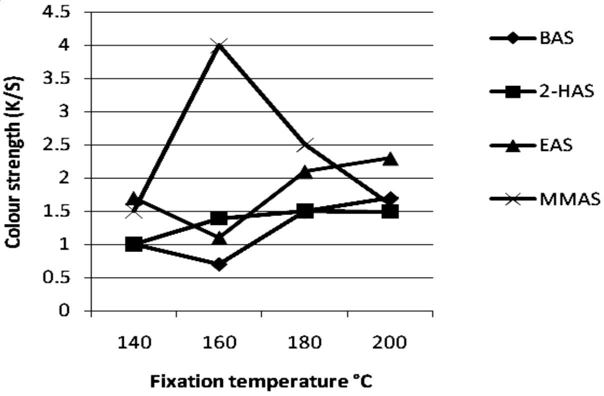

Fig. 7. Effect of the type of binders used on the colour strength of screen printed polyester fabrics using 3 % imperon brilliant red B, the time of fixation is 2 min

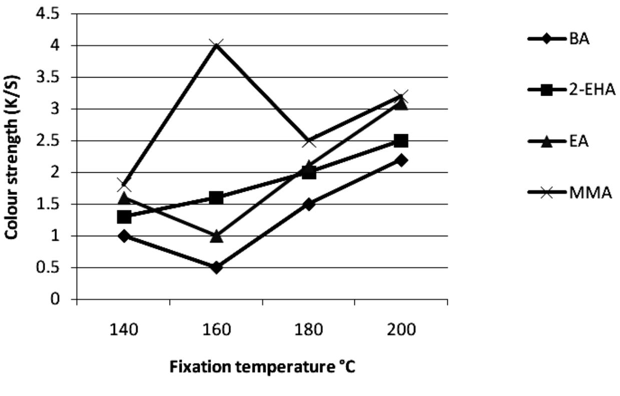

Fig. 8. Effect of the type of binders used on the colour strength of screen printed polyester fabrics using 5 % imperon brilliant red B, the time of fixation is 2 min

based on MMA a binder in printing paste containing 3 % imperon red B, respectively. This may be due to either the difference in the structure of the binder used or the amount of unsaturation groups found in the binders which is responsible for fixation of the dye through the polymerization process that happened to these oligomers *i.e.* binders.

Fastness properties: Table-3 shows the colour strength and overall fastness properties of screen printed natural and synthetic fabrics using synthetic styrene acrylate based on EA as a thermal curable binder used in preparing printing paste containing 3 % imperon brilliant red B.

TABLE-3
COLOUR STRENGTH AND OVERALL FASTNESS PROPERTIES OF SCREEN PRINTED NATURAL AND MAN-MADE FABRICS USING SYNTHESIS STYRENE ACRYLATE BASED ON EITHER EA, 2- EHA, BA AND MMA AS THERMAL CURABLE BINDERS IN PRINTING PASTE USING 3% IMPERON BRILLIANT RED B, THE TIME OF FIXATION IS 2 MIN

Binder used	Type of fabric colour strength	Rubbing fastness		Washing fastness			Perspiration fastness					
							Acidic			Alkaline		
				Staining			Staining			Staining		
		Dry	Wet	Cotton	Polyester	Alt.	Cotton	Polyester	Alt.	Cotton	Polyester	Alt.
EA	Cotton	4	4	3	4	2	4	4	3	4	4	3
2-EHA		4-5	3	4	4	4	5	5	5	5	5	5
BA		3-4	3	4	4	4	5	5	5	5	5	5
MMA		3-4	3-4	3-4	4-5	4	5	5	5	5	5	5
EA	Polyester	3-4	3-4	3	4	2	4	4	4	4	4	4
2-EHA		3-4	3-4	3-4	4	2	4	5	4	4	4	4
BA		3-4	3	4	4	3	4-5	5	4-5	4-5	4	4
MMA		3-4	3	4	4-5	5	5	5	5	5	5	5

It is clear from the data in Table-1 that the K/S and overall fastness properties not only depend on the type of binder used in printing paste but also on the type of textile fabric printed. The highest colour strength for cotton and polyester of printed fabric was obtained using MMA as a binder in printing paste and the fixation temperature was 160 ºC for 2 min and the lowest colour strength in case of cotton and polyester printed fabrics upon using EA the change in colour due to washing ranged from poor to good for all printed fabrics. The rubbing, washing and perspiration fastness ranged from good to excellent in case of using prepared binder. This was true irrespective of the nature of the binder used and/or the type of fabric printed.

Conclusion

These results show that some novel prepared aqueous binder of styrene acrylate based on having zero volatile organic compounds can be used safely for preparing printing paste for screen printing of cotton and polyester types of textile fabrics using pigment dyes.The highest K/S is obtained and the fastness properties range between good and excellent for samples printing using methyl methaacrylate styrene (MMA) based. This is true irrespective of the type of printed fabric. The lowest K/S is obtained in case of using ethyl acrylate styrene (EA) as a commercial binder. The binder of 2-ethylhexylacrylate (2-EHA) gives K/S better than the binder of butyl acrylate styrene (BA) for two types of printed fabrics.

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(*Received*: 20 November 2008; *Accepted*: 8 April 2009) AJC-7404