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RESEARCH ARTICLE

POLYHEXAMETHYLENE BISGUANIDINE: A NEW ANTIMICROBIAL AGENT FOR TEXTILE APPLICATIONS

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ABSTRACT

Polyhexamethylene Bisguanidine (PHMBG), a new compound with potential antibacterial activity was used as additive in the dyeing of cotton, wool and polyacrylonitrile fibres. The fastness properties and colour coordinates of the dyed samples were measured. The antibacterial agent applied by exhaustion with after treatment of the dyed fabrics did not affect the fastness properties of the dyeings while the colorimetric data of the dyed samples were slightly affected. The antibacterial activity of the samples treated with PHMBG as well as their stability against wet treatments was assessed and found to be excellent.

Abbreviations: PHMBG (polyhexamethylene bisguanidine), PAN (polyacrylonitrile), CC (colour change), CS (colour staining), omf (on mass fibre), D.O. 34 (Direct Orange 34), A.B.194 (Acid Black 194), B.B. 41 (Basic Blue 41).

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INTRODUCTION

During the last decades there has been a growing popularity in the preparation of textile products with active agents as additives. Incorporating successfully an active ingredient (e.g. antimicrobial, fragrance) in a textile article is a challenge to the producer. It gives the possibility of producing innovative personalized finished articles reducing the production stages and minimizing waste water and energy consumption. Among the numerous applications, there has been a growing interest in the development of bio-active textile materials with antimicrobial properties. Application of natural antimicrobial agents on textiles dates back to antiquity, when the ancient Egyptians to preserve mummy wraps. Natural antimicrobials were used to inhibit the growth of bacteria and mould in the fabric (Gyawali and Ibrahim, 2014; Joshi *et al*., 2009). The rapid growth in technical textiles and their end uses has generated many opportunities for the application of innovative finishes of textile materials. Novel finishes of high added value for apparel fabrics are greatly appreciated by a more discerning and demanding consumer market for health and hygiene.

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Textile materials in contact with body provide the ideal environment for growth and multiplication of pathogenic microbes leading to objectionable odour, dermal infection, product deterioration, allergies and other related diseases. These factors necessitate the development of methods to impart antimicrobial resistance to textiles with all the usual desirable characteristics of textiles, as these textile materials find extensive use in different sectors related to healthy and hygienic life style apart from the conventional apparel usage. To be successful in the marketplace, these finishes should be durable and have selective activity towards undesirable organisms (Yang, 2000; Gao, 2008; Purwar, 2004; Alonso, 2009). Use of such finishes will give to the finished article not only the desired colour design but additional properties which will increase the added value of the final article. A wide range of textile materials based on cotton, polyester, polyamide, wool etc are used to produce a variety of products from home textiles, floor coverings, outdoor fabrics, hosiery, surgical gowns etc. The above polymers are very susceptible to microbial attack resulting in odors, staining, discoloration and deterioration of the material itself. The conferred antimicrobial treatments ideally will offer protection against a variety of bacteria such as Gram negative bacteria e.g. pseudomonas aeruginosa, klebsiella, salmonella etc and Gram positive bacteria such as staphylococcus streptococcus, yeast etc.

The treated products should also resist fungi development such as: aspergillus niger, aspergillus flavus, penicillium funiculosum, chaetomium globosum, etc. Protection can also be offered against the new plague of the medical industry MRSA (Methicillin Resistant Staphylococcus Aureus**)** commonly found in hospitals and intensive care units (Appendinia and Hotchkiss, 2002). In continuation to our previous work on the use of several additives (fragrances, antimicrobials, optical brighteners) in conventional (dyeing) and novel (digital printing) textile applications (Karanikas *et al*., 2012; Karanikas *et al*., 2013; Karanikas *et al*., 2012) polyhexamethylene bisguanidine (PHMBG), a new compound with potential antibacterial activity was used as additive in the dyeing of cotton, wool and polyacrylonitrile fibres. The fastness properties and colour coordinates of the dyed samples were measured and the antibacterial activity of PHMBG adsorbed on the dyed fabrics was assessed.

MATERIALS AND METHODS

Materials

Unbleached greek cotton fabric without any treatment was used. Commercially available, lightweight (190 gm^{-2}) wool serge, kindly supplied by KYKE Hellas (Greece) and commercially available polyacrylonitrile fabric were used throughout this work. The dyes CI Direct Orange 34 1, CI Acid Black 194 2, CI Basic Blue 41 3 (Yorkshire Farben GmbH) were used for the dyeing of cotton, wool and polyacrylonirtile fabrics respectively. Polyhexamethylene bisguanidine 4 was supplied from Thomson Research Associates (Figure 1). As dyeing auxiliaries were used: sodium sulfate (Merck), acetic acid (Riedel-de-Haen), sodium chloride (Merck) and sodium carbonate (Merck).

Exhaustion of PHMBG

Isothermal exhaustion process of PHMBG on cotton, wool and acrylic fabric Isothermal PHMBG exhaustion curves were performed in a liquor ratio 1:20 and 2% o.m.f. PHMBG for the three fibres under the following conditions:

Cotton: T= 50, 98 ^oC; pH= 3, 4.8, 10.5; exhaustion values were measured at time intervals 1, 2, 4, 6, 8 and 16h. (Figure 3)

Wool: T= 50, 98^oC; pH= 3, 4.8; exhaustion values were measured at time intervals 1, 2, 4, 6, 8 and 16h. (Figure 4)

Polyacrylonitrile: T= 50, 98 ^oC; pH= 3, 4.8; exhaustion values were measured at time intervals 1, 2, 4, 6, 8h. (Figure 5).

Exhaustion values were calculated by measuring spectrophotometrically the absorbance of the compound at its λ_{max}= 193,4nm in the initial bath and the bath after treatment using the equation:

$$E_{\%} = \frac{(A_0 - A_t)}{A_0} \times 100$$, where:

A_0: initial bath absorbance at λ_{max}
A_t: bath absorbance at λ_{max} at time t

Determination of the exhaustion of PHMBG bath after treatment of the dyed fibres This was done with 0.25, 0.5 1.0, 2.0 and 4.0% o.m.f. PHMBG heating the dyed fabrics at 40 ^oC, pH 4.8 in a liquor ratio 1:20 for 30min.

Dyeing

Dyeings were carried out with a liquor ratio 1:20 and depth of dyeing 2 % omf.

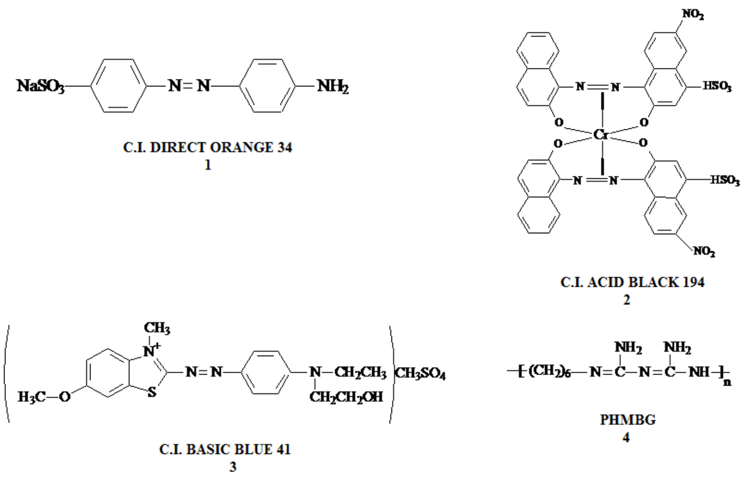

Figure 1. Structure of dyes and the active agent used

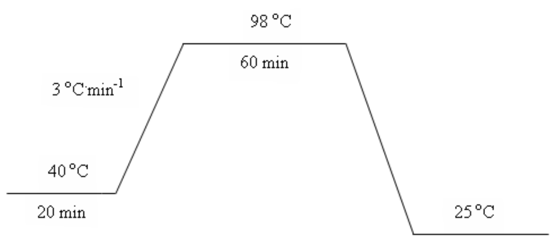

Figure 2. Dyeing process of cotton, wool, acrylic fibres

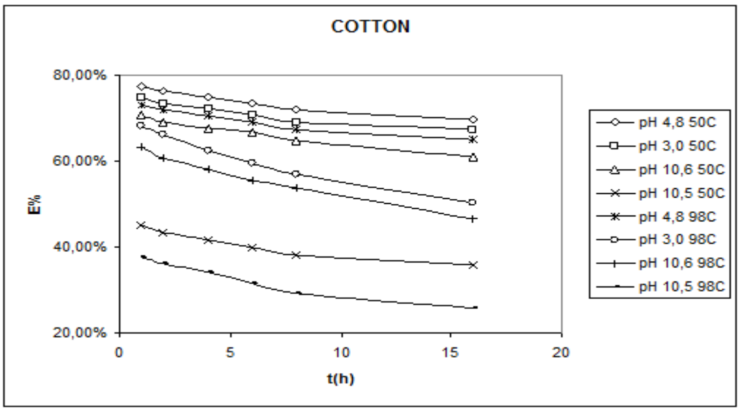

Figure 3. Isothermal PHMBG exhaustion curves on cotton fabric

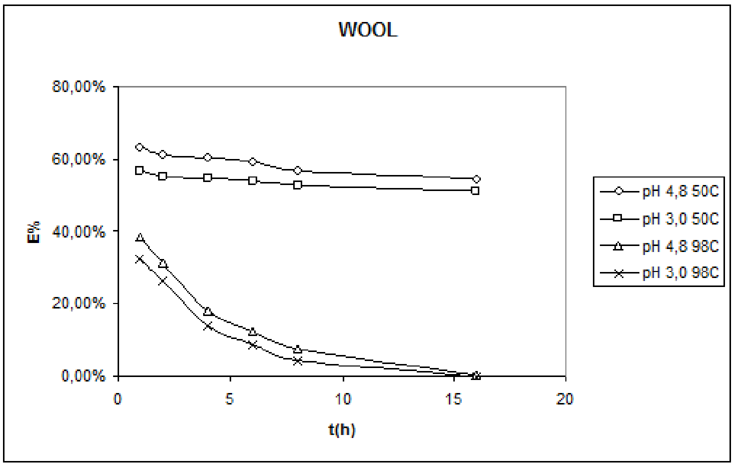

Figure 4. Isothermal PHMBG exhaustion curves on wool fabric

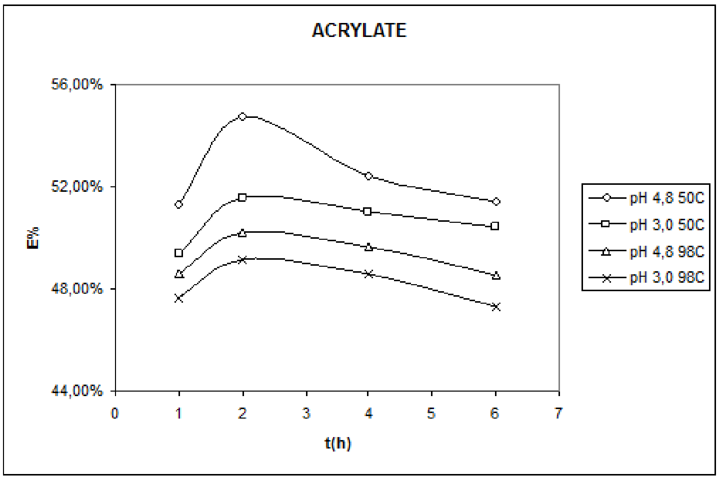

Figure 5. Isothermal PHMBG exhaustion curves on polyacrylonitrile fabric

The dyeing process is given in Figures 2a, 2b, 2c for the cotton, wool and polyacrylonitrile dyeing respectively (Figures 2a-2c). Application of PHMBG was made by exhaustion with after treatment of the dyed samples with 0.25, 0.5, 1.0, 2.0, 4.0% o.m.f. PHMBG.

Fastness tests

Wash fastness of the prints and dyeings was carried out according to BS1006:1990CO2 test, whereas light fastness was carried out according to BS1006:1990BO2 test (Standard Methods for the Determination of the Colour Fastness of Textiles and Leather, 1990).

Colour measurements

The reflectance values of the dyeings were measured using a Macbeth CE 3000 spectrometer under D65 illumination, 10 standard observer with UV included and specular component excluded. The CIE1976 L*, a*, b*, C*, h* coordinates and the K/S values were calculated from the reflectance values at the appropriate λmax (λmax Direct Orange 34=440 nm, Acid Black 194= 580 nm, Basic Blue 41= 600 nm).

Quantitative antibacterial assessment of the dyed cotton sample treated with triclosan

This was done by Thomson Research Association, Canada, according to ISO 20743:2007 as follows:

- A piece of the sample was placed into a container with a lid.
- A 0.2ml inoculum of K. pneumoniae was placed in microdroplets on the surface of the sample. 0.05% Tween 80 was added to the inoculum as a wetting agent.
- The specimen was incubated 18h at 37 ^oC.
- 20ml of Letheen broth was added to the container and shaken. The bacteria in the liquid were quantified by using a series of dilution plates.

RESULTS AND DISCUSSION

Exhaustion of PHMBG

In order to conclude the optimal application conditions of the PHMBG on cotton, wool and acrylic fibres the isothermal PHMBG exhaustion curves on cotton, wool and polyacrylonitrile fabric are given (Figures 3-5). Figures 3-5 show the isothermal (50 ^oC, 98 ^oC) PHMBG exhaustion values at various time intervals for the undyed cotton, wool and acrylic samples respectively. From figures 3-5 it is concluded that temperature 50 ^oC, significantly lower than cotton dyeing temperature 98 ^oC and pH 4.8 are the optimal conditions for the exhaustion of PHMBG. The highest exhaustion value is observed at the 1h measurement being reduced with time in all cases.

The high exhaustion value 77.3% of PHMBG at these conditions could be attributed to the high substantivity of PHMBG to the cellulose fibre. The linear structure of the molecule and the presence of amino groups capable of forming hydrogen bonds are favouring the adsorption of PHMBG on the fibre. The low exhaustion values observed at pH 10.5 where the hydroxyl groups of cellulose are dissociated, indicate that non polar bonds, hydrogen bonds, Van der Vaals forces are responsible for the PHMBG adsorption on the cellulose fibre (Figure 3). In the case of the isothermal exhaustion process on wool fibre (Figure 4) exhaustion values are lower than the corresponding on cotton and temperature increase to 98 ^oC (wool dyeing temperature) results in a significant decrease in the exhaustion value.

PHMBG in acidic pH is cationic, thus polar forces between the positively charged amino groups of the molecule and the carboxylic anions of the wool fibre are responsible for the PHMBG adsorption on the above fibres (Influence of Fibre Structure on Dye Uptake in “The Theory of Coloration of Textiles, 1975). Regarding polyacrylonitrile fibres acidic comonomers containing sulfonic, phosphoric or carboxylic acid groups (e.g. sodium vinyl benzene sulfonate) which confer substantivity for basic dyes or cationic compounds in general of the acrylic fibre are responsible for the PHMBG adsorption on the these fibres (Figure 5) (Influence of Fibre Structure on Dye Uptake in “The Theory of Coloration of Textiles, 1975).

Table 1. Exhaustion values of PHMBG after treatment of the undyed/dyed samples at 40 ^oC and pH 4.8

Fibre	Dye	PHMBG %	E% (dyed)	E% (undyed)
		0.25	64.04	77.27
		0.5	71.31	75.34
COTTON	D.O. 34	1.0	75.44	76.88
		2.0	75.88	76.39
		0.25	64.04	56.90
		0.5	63.97	57.36
WOOL	A.B. 194	1.0	63.47	58.77
		2.0	58.78	60.06
		4.0	36.90	60.76
		0.25	73.15	86.90
		0.5	73.20	72.29
PAN	B.B. 41	1.0	66.90	66.24
		2.0	54.52	54.58
		4.0	34.35	29.90

Table 2. Wash and light fastness values of the dyed samples with/without active agent

Sample		Fastness							
			Wash						
	Fibre/ % PHMBG	Light	Colour Change (CC)	Colour Staining (CS)					
				Acetate	Cotton	PA	PES	PAN	Wool
1.1	COTTON/ 0	>7	5	5	2	5	5	5	5
1.2	COTTON/ 0.25	>7	5	5	2	5	5	5	5
1.3	COTTON/ 0.5	>7	5	5	2	5	5	5	5
1.4	COTTON/ 1.0	>7	5	5	2	5	5	5	5
1.5	COTTON/ 2.0	>7	5	5	2	5	5	5	5
2.1	WOOL/ 0	>7	5	5	5	4-5	5	5	5
2.2	WOOL/ 0.25	>7	5	5	5	4-5	5	5	5
2.3	WOOL/ 0.5	>7	5	5	5	4-5	5	5	5
2.4	WOOL/ 1.0	>7	5	5	5	4-5	5	5	5
2.5	WOOL/ 2.0	>7	5	5	5	4-5	5	5	5
2.6	WOOL/ 4.0	>7	5	5	5	4-5	5	5	5
3.1	PAN/ 0	4-5	5	5	5	5	5	5	5
3.2	PAN/ 0.25	4-5	5	5	5	5	5	5	5
3.3	PAN/ 0.5	4-5	5	5	5	5	5	5	5
3.4	PAN/ 1.0	4-5	5	5	5	5	5	5	5
3.5	PAN/ 2.0	4-5	5	5	5	5	5	5	5
3.6	PAN/ 4.0	4-5	5	5	5	5	5	5	5

Table 3. Colorimetric data and colour strength values for the cotton, wool and acrylic dyeing

Sample	Fibre/% PHMBG	K/S	λmax (nm)	L*	a*	b*	C*	H*
1.1	COTTON/ 0	21.64	440	50.21	35.20	56.06	66.20	57.87
1.2	COTTON/ 0.25	21.84	440	52.30	37.29	59.58	70.29	57.95
1.3	COTTON/ 0.5	20.94	440	52.04	37.34	58.61	69.49	57.50
1.4	COTTON/ 1.0	24.52	440	50.50	38.42	59.00	70.41	56.93
1.5	COTTON/ 2.0	23.29	440	51.17	37.22	58.74	69.54	57.64
2.1	WOOL/ 0	21.60	580	14.35	0.67	-1.03	1.23	302.89
2.2	WOOL/ 0.25	20.06	580	13.71	0.64	-1.03	1.22	301.75
2.3	WOOL/ 0.5	22.49	580	18.97	0.02	-3.49	3.49	270.28
2.4	WOOL/ 1.0	20.19	580	16.11	0.68	-1.25	1.42	298.66
2.5	WOOL/ 2.0	22.68	580	15.37	0.60	-3.12	3.17	280.88
2.6	WOOL/ 4.0	22.60	580	15.69	0.35	-2.83	2.85	277.01
3.1	PAN/ 0	33.89	600	31.93	2.61	-42.97	41.64	274.10
3.2	PAN/ 0.25	32.38	600	31.86	3.41	-36.10	36.26	275.39
3.3	PAN/ 0.5	34.78	600	28.36	2.56	-32.85	32.95	274.46
3.4	PAN/ 1.0	34.52	600	31.35	0.92	-32.61	32.62	271.61
3.5	PAN/ 2.0	35.05	600	30.84	0.48	-32.42	32.43	270.84
3.6	PAN/ 4.0	35.19	600	32.08	-3.16	-31.28	31.44	264.24

Table 4. Quantitative Assessment of PHMBG activity against K. pneumoniae

Quantitative Assessment of Activity-ISO 20743: 2007 K. pneumoniae	
Sample Description	**% Reduction**
2% PHMBG, 40 C, COTTON, pH 4.8	>99.9%
2% PHMBG, 40 C, WOOL, pH 4.8	>99.9%
2% PHMBG, 40 C, PAN, pH 4.8	>99.9%

After 20 washes

Quantitative Assessment of Activity-ISO 20743: 2007 K. pneumoniae	
Sample Description	**% Reduction**
2% PHMBG, 40 C, COTTON, pH 4.8	97.0%
2% PHMBG, 40 C, WOOL, pH 4.8	70.5%
2% PHMBG, 40 C, PAN, pH 4.8	96.7%

Since dyeing temperature 98 ^{o}C does not favour exhaustion as it was concluded from the isothermal treatment processes the application of PHMBG on the fabrics was made by exhaustion with after treatment of the dyed samples at 40 ^{o}C and pH 4.8 with PHMBG amounts 0.25, 0.5, 1.0, 2.0 and 4.0% o.m.f.. The results are given in table 1. Exhaustion values of PHMBG after treatment of the undyed samples at the same conditions are also given in Table 1.

The highest substantivity of the cationic PHMBG for cotton is confirmed. Even with the highest PHMBG amount 2.0% omf the % exhaustion value remains high 75.88%, while for wool and acrylic fibre the % exhaustion value is reducing with increasing PHMBG amount indicating a gradual saturation of the fibre. The % exhaustion values are higher for the undyed samples indicating a competition of the antibacterial agent to the dye molecules which reduce the adsorption of the PHMBG molecules on the fibre especially at high amounts 2.0 and 4.0 % o.m.f. of PHMBG.

Fastness properties

The wash and light fastness of all the dyed and aftertreated samples 1.1-1.5, 2.1-2.6 and 3.1-3.6 (numbering and description of the dyed and aftertreated samples is given in Table 2) was measured and the results are given in Table 3. Table 3 shows that the application of PHMBG by exhaustion on the dyed samples did not affect the light and wash fastness The dyed samples. The light fastness of all cotton and wool samples is excellent (score >7 of the blue standard scale 1-8) while light fastness values of the acrylic samples are medium (score 4-5 of the blue standard scale 1-8).

Wash fastness values are very good to excellent in most cases (4-5 to 5 in most cases of the grey scale 1-5) with the exception of cotton fibre which gives a low colour staining value on cotton (2 of the grey scale 1-5). This could be attributed to the probable low substantivity of Direct Orange 34 for the cellulose fibre due to its relatively low molecular weight resulting in a more superficial adsorption of the dye on cotton sample and its easier elimination. The desorpted dye was staining preferentially the cotton in the multifibre strip, without affecting the colour change value which is excellent (score 5 of the grey scale 1-5) in all cases.

Colour measurement

Table 3 shows the relevant colorimetric data and colour strength values for the cotton, wool and acrylic dyeings. L*, a*, b*, C*, H* co-ordinates and the K/S values were calculated from the reflectance values at the appropriate λmax (440, 580 and 600nm for CI Direct Orange 34, CI Acid Black 194 and CI Basic Blue 41 respectively) (Colorimetry and the CIE System in Colour Physics for Industry, Society of Dyers and Colourists, 1997).

K/S values of the dyed samples are high in all cases indicating the suitability of each dye for the corresponding fibre: The linear structure of C.I. Direct Orange 34 **1** and the presence of amino group capable of forming hydrogen bonds and the hydrophilic -$NaSO_3$ group are favouring its adsorption on the fibre.

C.I. Acid Black 194 **2** with two sulfonic groups is anionic, thus polar forces between the positively charged amino groups of the wool fibre are responsible for its adsorption on the above fibre (Influence of Fibre Structure on Dye Uptake in "The

Theory of Coloration of Textiles, 1975). Regarding polyacrylonitrile fibres acidic comonomers containing sulfonic, phosphoric or carboxylic acid groups (e.g. sodium vinyl benzene sulfonate) which confer substantivity for basic dyes or cationic compounds in general of the acrylic fibre are responsible for the adsorption of C.I. Basic Blue 41 3 on the the polyacrylonitrile fibre (Fig. 5) (Influence of Fibre Structure on Dye Uptake in "The Theory of Coloration of Textiles, 1975). No significant effect on the K/S values for both blue and yellow samples has been observed on dyed polyester and polyamide samples with the inclusion of the active agents as it was expected since the antibacterial agent was applied by after treatment of the dyed samples.

Antibacterial measurements of the dyed samples

The antibacterial activity was tested against a negative gram bacterial klebsiella pneumonia. The antibacterial agent PHMBG showed high levels of antibacterial activity as this is expressed by the high values % bacterial area reduction in Table 5. The bacterial free area is approaching almost 100% of the treated area for k. pneumoniae for the cotton substrate with 2% omf PHMBG. The same test was performed after 20 washings (sample 2) with excellent results (% reduction of k. pneumoniae 97%) indicating that PHMBG is not eliminated from the substrate after repeated wet treatments thus fulfilling the requirements of an antibacterial additive.

Conclusion

Polyhexamethylene bisguanidine (PHMBG), a new compound with potential antibacterial activity was used as additive in the dyeing of cotton, wool and polyacrylonitrile fibres. The fastness properties and colour coordinates of the dyed samples were measured. The antibacterial agent was applied by exhaustion with aftertreatment of the dyed fabrics according to the optimal application conditions of PHMBG on cotton, wool and acrylic fibres concluded from the isothermal PHMBG exhaustion curves on cotton, wool and polyacrylonitrile fabric made and the study on the optimal exhaustion condition carried out. PHMBG applied with aftertreatment on the dyeings did not affect the fastness properties of the dyeings while the colorimetric data of the dyed samples were slightly affected. The antibacterial activity of the samples treated with PHMBG as well as their stability against wet treatments was assessed and found to be excellent.

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