Bulgarian Chemical Communications, Volume 49, Special issue L (pp.181-186) 2017

Investigation on the influence of reactive dyes over the colour stability of offset printing paper during ageing

D. A. Todorova*, P. M.Miladinova

University of Chemical Technology and Metallurgy, 8 Kl. Ohridski, 1756 Sofia, Bulgaria

Received November 21, 2016; Accepted May 8, 2017

Contrary to the general belief that coloured papers are mainly used in the field of hygiene and tissue papers, nowadays during the printing process with the new digital technology some of the specialists in the printing and publishing industry prefer to produce special books and journals with specifically coloured paper. Therefore, dyeing of offset paper is reasonable. The reactive dyes are well known mainly as a textile dyes and they have only limited use in paper production. They are capable of forming covalent dye-polymers bonds, for instance, with the hydroxyl groups of cellulose. The purpose of this study was to investigate the influence of reactive dyes over the colour stability during the accelerated ageing of the paper, both at dry heat and at exposure to light.

In this experiment were used two laboratory synthesized reactive dyes, derivatives of chlorotriazine and one of them contains a stabilizer fragment. Dyes were used in the composition of offset printing paper with a fibre content of bleached softwood and hardwood pulp in a ratio of 1:1. The paper was sized with alkyl ketene dimer and as filler was used natural calcium carbonate. The optical properties - L*C*h* from the CIE Lab colour space have being examined before and after the accelerated ageing of the resulting paper samples.

As a result of the studies carried out it was found out that with both reactive dyes were obtained paper samples with similar colour shades, uniform colouring and stable colour, distinguished by stability under thermal and light accelerated aging.

Key words: accelerated ageing of paper, thermal ageing, light ageing, reactive dyes, optical properties

INTRODUCTION

Contrary to the general belief that coloured papers are mainly used in the field of hygiene and tissue papers, nowadays during the printing process with the new digital technology some of the specialists in the printing and publishing industry prefer to produce special books and journals with specifically coloured paper. Therefore, dyeing of offset paper is reasonable and the use of reactive dyes would have benefits, both for the properties and for the colour stability during ageing of the paper. Generally, paper is colour by dyes of different chemical nature – inorganic pigments; synthetic organic pigments; basic, acid, direct dyes and others.

The reactive dyes are well known mainly as a textile dyes and they have only limited use in paper production. They have been tested in the late 1800s [1]. The first reactive dye is synthesized by IG Farben in 1932, but it first appeared commercially in 1956, after their invention in 1954 by Rattee & Stepheness at the Imperial Chemical Industry (ICI), Dyestuffs Divion site in Bleckley, Manchetor, UK [2,3]. They stand out from other dyes by their ability to make covalent bonds between carbon atoms of the dye reactive group and oxygen atoms of pulp hydroxyl groups under alkaline conditions [4]. Reactive dyes are divided, according to their structure of reactive group, in haloheterocycle and vinyl sulfone based dyes, which react with cellulose through nucleophilic substitution and addition mechanisms, respectively. Commercially, the widest used systems are: vinyl sulfone, monochlorotriazine, bifunctional dyes, difluoro chloropyridine, monofluoro triazine and dichlorotriazine. In addition to reacting with fibre, reactive dyes also react with water (dye hydrolysis) in a form which cannot bound to cotton, but behaves as a substantive dye and affects colour fastness, when is used on fabric. The most important parameter affecting exhaustion and „fixation“ of reactive dyes are temperature, salt and alkali concentration and liquid ratio [4].

Because of the limited use of reactive dyes in the paper dyeing process, there are not so much results about the properties of the paper suspension, paper white waters and paper properties.

The quality and long-term stability of paper materials produced from cellulosic fibres with various additives are determined by the extent of oxidative and hydrolytic reactions taking place upon ageing. These processes may considerably reduce the physicomechanical and chemical properties of

*) To whom all correspondence should be sent:
E-mail: todorova.dimitrina@uctm.edu

paper, resulting in damage to paper structure, an increase of brittleness, and finally, a total loss on material quality. The hydrolytic and oxidative processes are related to each other, and are affected by various intrinsic factors (sizing, filling, adhesives, the presence of acid groups, metal ions, lignin, etc.) and extrinsic factors (storage conditions, temperature, humidity, the presence of oxygen, light and environmental impurities) [7].

The purpose of this study was to investigate the influence of new reactive dyes over the colour stability during the accelerated ageing of paper, both at dry heat treatment at 105 °C and at exposure to light with intensity of 765±75W/m^2 and wavelength of 290-800nm.

EXPERIMENTAL

The investigations were carried out with laboratory obtained paper samples (70g/m^2) from bleached hardwood and softwood pulp in proportion 1:1, with beating degree of 42°SR (Schopper Riegler). The paper samples were sized with Alkyl Ketene Dimer (AKD) – 2% from o.d.f., filled with natural calcium carbonate ($CaCO_3$) – 20% from o.d.f. and as a retention additive (RA) was used modified poly acryl amide with cationic charge in consumption 0,05% from o.d.f.

The two examined dyes were laboratory synthesized red reactive dyes. The compounds are monoazo reactive dyes whose chromophore is an orange acid dye, prepared by diazotization of the amino C acid and subsequently coupling with I acid in slightly alkaline medium. Reactive group (chlorine atom) was introduced into the chromophore by reaction of the acid orange dye with cyanuric chloride and the dichlorotriazine reactive dye was obtained. In the subsequent step by a reaction of the last one with 4-amino-2,2,6,6-tetramethylpiperidine or ammonia the monochlorotriazine reactive orange dyes (1) and (2) were obtained (Fig.1).

The tetramethylpiperidine fragment in the molecule acts as a stabilizer fragment and its introduction was done with purpose - increment of the colour fastness to light (photo-stability). It was expected that the paper dyed with this dyes exhibit also a greater photo-stability. This assumption was made based on the fact that the dyed fibres (cotton and wool) and chemically coloured polymers showed high photo-stability [5,6].

The consumption of Reactive Dye 1 (RD1) and Reactive Dye 2 (RD2) in the paper was 0,2%, 0,4%, 0,6% from o.d.f.

The obtained paper samples were examined for their optical properties – colour coordinates L*, C* and h* before and after the accelerated ageing, by Frank – PTI spectrophotometer / D65_10.

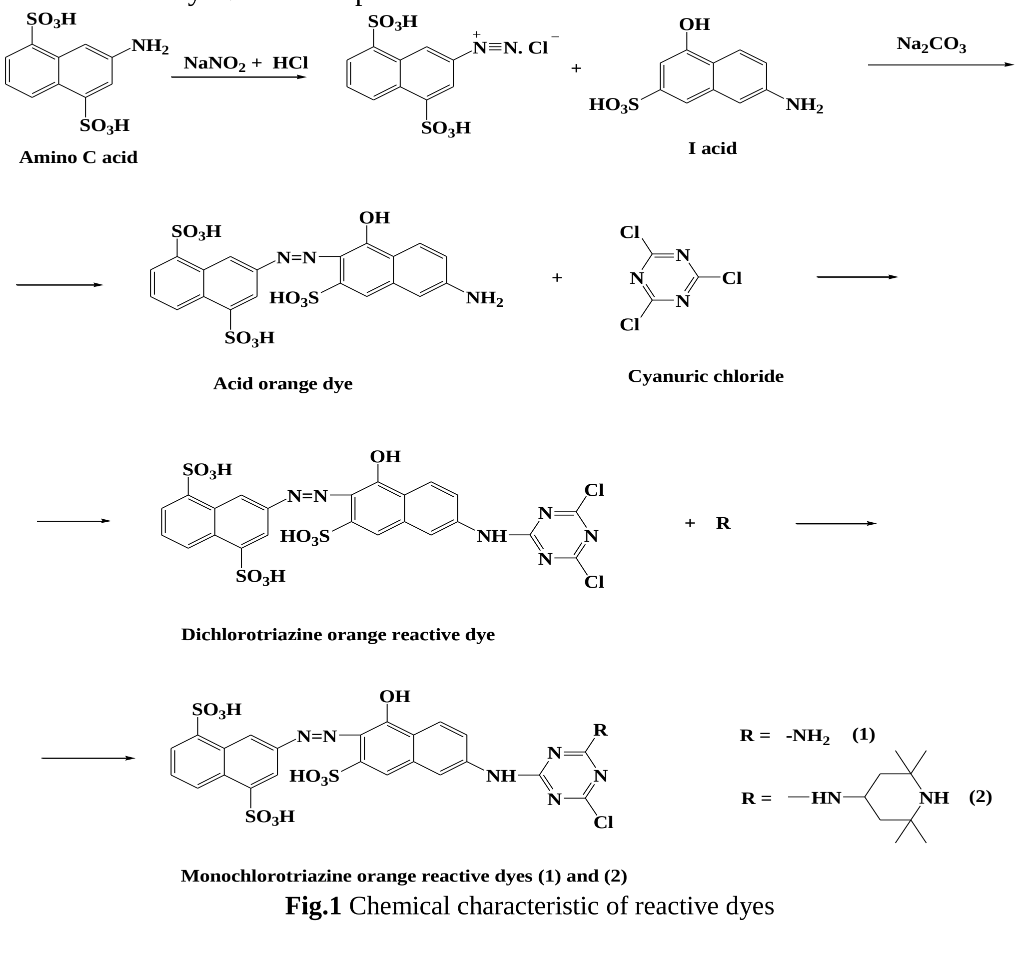

Fig.1 Chemical characteristic of reactive dyes

The thermal ageing was conducted according to ISO 5630-1:2014 [8] at temperature of 105 °C, and duration of 36h.

The light ageing is being conducted according to ISO 5630-7:2014 [9], by exposure to light with intensity of 765±75W/m^2 and wavelength of 290-800nm and duration of 48h.

The CIE L*c*h* Colour Space is in the form of a sphere and there are three axes; L*, C* and h* [10].

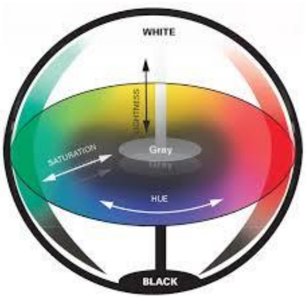

Fig.2 The CIE L*c*h* Colour Space.

The L* axis represents *Lightness*, brightness and the brilliance of the paper. This is vertical; from 0, which has no lightness (i.e. absolute black), at the bottom; through 50 in the middle, to 100 which is maximum lightness (i.e. absolute white) at the top. Just like CIELab, the lighter the colour, the higher the value.

The C* axis represents *Chroma* or 'saturation'. This ranges from 0 at the centre of the circle, which is completely unsaturated (i.e. a neutral grey, black or white) to 100 or more at the edge of the circle for very high Chroma (saturation) or 'colour purity'. Chroma, or saturation, describes where a colour falls between the centre and the edge of the sphere. Lower numbers near the centre are more grey and have very little chroma, while higher numbers are purer and saturated.

The h* axis represents *Hue*. The units are in the form of degrees° (or angles), ranging from 0° (red) through 90° (yellow), 180° (green), 270° (blue) and back to 0 and all of the colours that fall in-between. [10]. The L*C*h° colour model is very useful for coloured papers.

RESULTS & DISCUSSION

The process of natural ageing of paper is too slow to permit observing changes in a reasonable time frame. Thus, different methods of accelerate ageing of paper under dry heat and light exposure have often been used to speed up the process of physic-mechanical and optical changes of properties in the paper. The hydrolytic degradation has been looked as the most important reason for the loss of strength properties of the paper and the lignin content as the most important factor for light ageing. In the present study, the raw material was bleached pulp, so that the lignin cannot be of an essential factor for the colour change during thermal and light ageing.

The colours with the same hue can further vary - can be very bright and clear or dull and grey - e.g. strong blatant, brilliant red or mat, increscent red. This is characterized by the colour parameter C* - colour, saturation, intensity, purity of tone. With increasing C*, increases the colour growing, intensity of colour. Similarly, chromaticity C *, the colours may in the same colour tone h * yet differ in their brightness L *.

Influence of the quantity and type of reactive dyes, on the colour parameters of the papers during accelerate thermal ageing

It is known, from the different previous publications, that three days (72h) of accelerated thermal ageing at 105ºC is equal to 25 years of natural ageing [11,12]. In view of the fact, that the received by us paper samples were from bleached cellulose and its thermal aging is most noticeable during the first six hours, we assumed that for the colour parameters longer aging than 36h was not necessary.

The colour coordinate - L*, which expresses the lightness, brightness and the brilliance of the paper, decreases with adding of both reactive dyes (Fig.3). The colour parameter variation with time is comparatively low, being most sensitive during the first 24 hours. The differences between both reactive dyes are small. But at 0,2% consumption of both RD, the lightness of the paper samples is nearly the same and it stayed stable after 36h accelerated thermal ageing. With increasing the dyes consumption and the duration of the thermal ageing, the colour of the paper samples is slightly getting lighter and the colour difference is getting bigger.

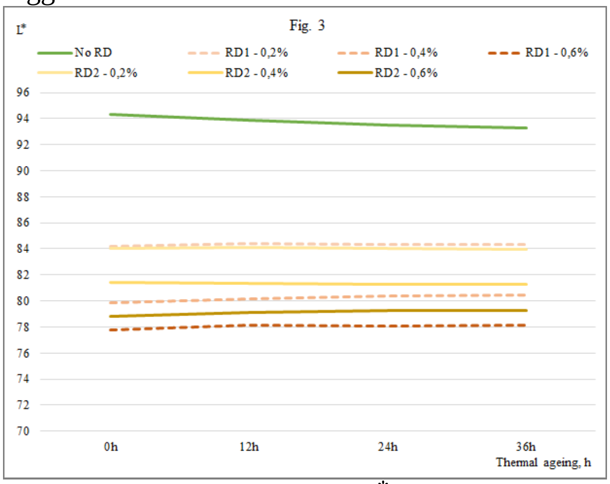

Fig. 3. Dependence of Lightness (L*) of the paper samples at different RD type and consumption, from the duration of the thermal ageing

The colour difference between the samples dyed with the two examined reactive dyes is nearly imperceptible for the human eye.

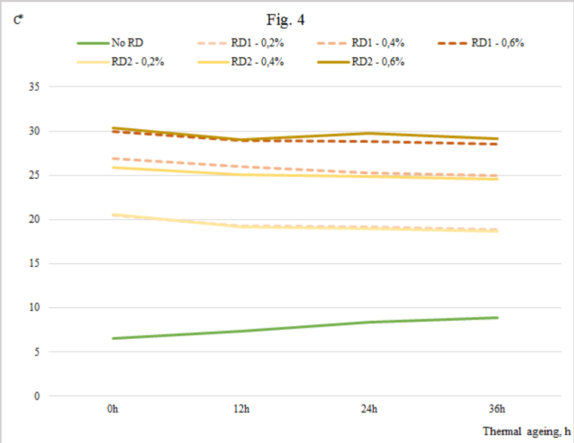

Fig. 4. Dependence of Chroma (C*) of the paper samples at different RD type and consumption, from the duration of the thermal ageing

As it is seen from Fig.4 and Fig.5, which represents the Chroma – C* and the Hue - h* of the papers samples, with both reactive dyes are obtained paper samples with uniform colouring, which is comparatively stable during thermal ageing. Relatively large changes in the parameter C* were observed at the higher consumption of both examined dyes (0.4% and 0.6%), while at consumption 0.2% the values for C* are almost the same.

Usually, the hue of the coloured paper samples is the most sensitive parameter during ageing and especially during the first 24h. As it is seen from Fig. 5 the difference between the colour of the paper at 0,4% and 0,6% consumption of the dye is less, than that at 0,2%. With increasing the RD consumption, the colour parameter h* is getting less susceptive of accelerated thermal ageing, i.e. the brighter the colour, the bigger the changes.

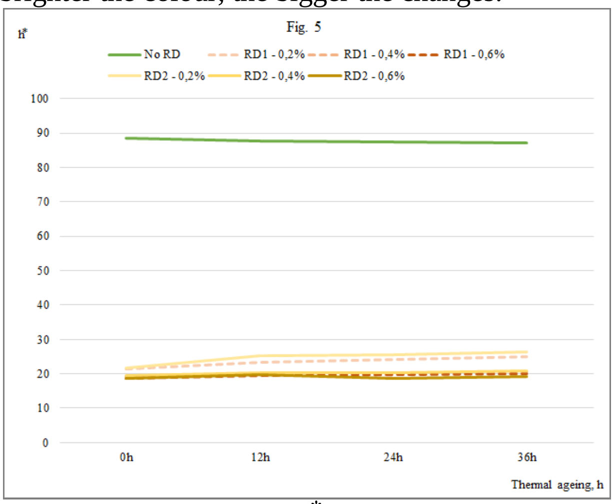

Fig. 5. Dependence of Hue (h*) of the paper samples at different RD type and consumption, from the duration of the thermal ageing.

Influence of the quantity and type of reactive dyes, on the colour parameters of the papers during accelerate light ageing

Light plays an important role in the natural ageing of paper. The effect of light on paper has been reviewed by several authors [13, 14] and a lot of experiments had been made during the natural conditions. Experimental results indicate that the mechanisms for aging with pollutants, light and heat are all different from each other and are also fibre dependent [15].

In our experiment the accelerated light ageing has been conducted in apparatus - Ametek Atlas MTS Suntest CPS+ Benchtop Xenon Exposure Environment Tester Chamber (Fig.6).

Fig. 6 Paper samples in the Suntest apparatus

The results for the colour parameters of the paper samples are shown on Fig.7, Fig.8 and Fig.9.

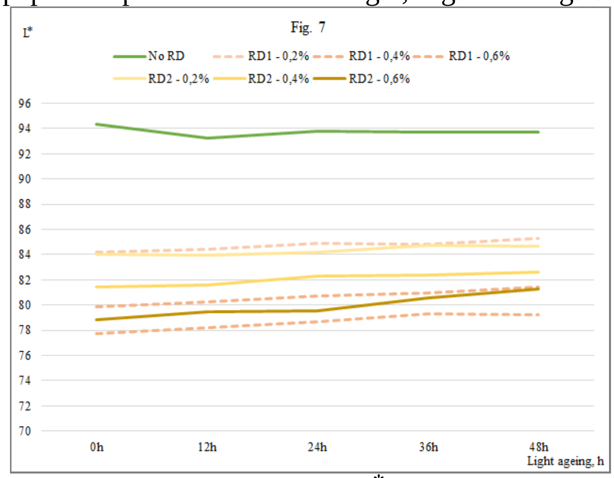

Fig.7. Dependence of Lightness (L*) of the paper samples at different RD type and consumption, from the duration of the light ageing

As it is seen from Fig.7, which represents the colour lightness of the paper samples, during the accelerated light aging, the parameter L* is amended even for paper without reactive dye, which shows the aggressiveness of this type of aging, compared to the thermal ageing. The first 24 hours of aging also shows most sensitive colour changes. From Fig.7 it is seen that the values of the parameter L* decreases, which means that the paper is getting darker. The results shown on Fig. 9, which represents the hue of the paper, shows that the colour is amended to the yellow hues. With further continuance of the light aging, the paper samples are becoming brighter again, which is associated with the burnout of the colour of the paper.

During the light aging of the paper samples, the largest variation is observed for the parameter C*, which represents the saturation of the paper. Fig.8 shows, that the paper samples lose colour saturation, because the values decreases, i.e. the colour is getting more faded. Unlike the thermal aging, here the changes during the ageing duration, are not so smooth and the susceptibility of RD2 is greater than that of RD1. The paper samples are losing their purity and become grey and turbid.

On Fig.9 is shown the variation of the hue parameter (h*) of the paper samples during accelerated light ageing. As it is seen, most stable was the colour of paper samples dyed with RD2, at consumption of 0.4% of the dye. Obviously at low quantities of the dyes, the colour of the paper samples is more sensitive to light aging, especially in presence of RD1, which do not contain a light-stabilizer fragment in its molecule.

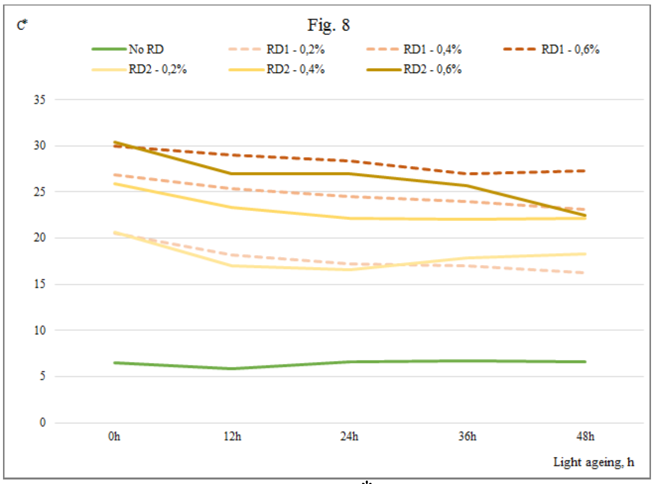

Fig. 8. Dependence of Chroma (C*) of the paper samples at different RD type and consumption, from the duration of the light ageing

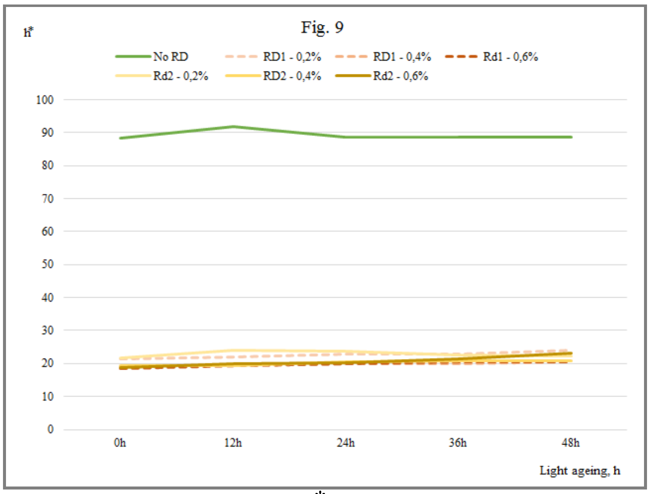

Fig. 9. Dependence of Hue (h*) of the paper samples at different RD type and consumption, from the duration of the light ageing

CONCLUSIONS

On the basis of the results of the studies carried out for dyeing wood free neutrally sized paper by two laboratory synthesized reactive dyes, using cationic polyacrylamide as retention additive and with a view of the complex influence on the colour stability during accelerated ageing the following conclusions can be made:

- With both reactive dyes have been obtained paper samples with uniform colouring.
- The colour difference between the samples dyed with the two examined reactive dyes are nearly imperceptible for the human eye.
- During the accelerated thermal aging, the changes of the colour are smaller and smoother.
- During the accelerated light aging, the changes in the colour are larger and have more variation in the parameters.
- Most variable colour parameter during accelerated aging is the chroma - C*.
- During the thermal aging, more stable over time is the colour characteristics of the paper samples dyed with RD1 and those of PD 2 are more stable during the light aging, demonstrating the positive effect of the presence of light-stabilizer fragment in its molecule.
- Most suitable in terms of colour stability is RD2 at 0,4% consumption.
- Both examined reactive dyes are suitable for dyeing of offset printing paper.

REFERENCES

1. H. Tappe, W. Helmling, P. Mischke, K. Rebsamen, U. Reiher, W. Russ, L. Schläfer, P. Vermehren "Reactive Dyes"in Ullmann's Encyclopedia of Industrial Chemistry, Wiley-VCH, Weinheim, (2000)
2. K. Venkataraman, The Chemistry of Synthetic Dyes, Vol. 7. Academic Press: New York, (1972).
3. Dyeing of cotton fabric with reactive dyes, textilelearner.blogspot.com, (2012).
4. N. Ristic, I. Ristic, *J. Eng. Fiber Fabrics*, **7**, 113, (2012).

5. P. Petrova-Miladinova, T. Konstantinova, *J. Univ. Chem. Technol. Met.*, **39**, 405 (2004).
6. T. Konstantinova, P. Petrova-Miladinova, *Dyes and Pigments*,, **67**, 63 (2005).

185

7. B. Havlínová, S. Katuščák, M. Petrovičová, A. Maková, V. Brezová, *J. Cultural Heritage*, **10**, 222 (2009).
8. ISO 5630-1:2014. Paper and board — Accelerated ageing — Part 1: Dry heat treatment at 105 °C, International Organization for Standardization, Geneva, Switzerland, (2014)
9. ISO 5630-7:2014. Paper and board — Accelerated ageing — Part 7: Exposure to light, International Organization for Standardization, Geneva, Switzerland, (2014)
10. H. Kipphan, „Hand Book of Print Media", Heidelberg, Springer, (2001)
11. X. Zou, T. Uesaka, N. Gurnagul, *Cellulose*, **3**, 243, (1996).
12. X. Zou, T. Uesaka, N. Gurnagul, *Cellulose*, **3,** 269 (1996).
13. S. Zervos, A. Moropoulou, *Int. J. Preservation Library Archival Materialc*, **27**, 219 (2006).
14. V. Bukovski, *Restaurator*, **21**, 55 (2000).
15. M. Area, H. Cheradame, *BioResources*, **6**, 5307 (2011).

ИЗСЛЕДВАНЕ НА ВЛИЯНИЕТО НА РЕАКТИВНИ БАГРИЛА ВЪРХУ СТАБИЛНОСТТА НА ЦВЕТА НА ОФСЕТОВА ХАРТИЯ ЗА ПЕЧАТ ПРИ СТАРЕЕНЕ

Д. А. Тодорова*, П.М.Миладинова

Химикотехнологичен и металургичен университет, бул. Климент Охридски №8, София 1756

Постъпила на 21 ноември, 2016 г.; приета на 8 май, 2017 г.

(Резюме)

Противно на общото схващане, че цветни хартии се използват главно в санитарно-хигиената областта, в днешно време в процеса на печат с новите цифрови технологии, някои от специалистите в полиграфическата индустрия предпочитат да произвеждат уникални книги и списания с специално оцветена хартия. Ето защо, багренето на офсетова хартия е разумно. Реактивните багрила са добре известни предимно като текстилни багрила и имат ограничено използване при производството на хартия. Те са способни да образуват ковалентни химични връзки (багрило-полимер), например с хидроксилните групи на целулозата. Целта на експеримента е да се изследва влиянието на реактивни багрила върху стабилността на цвета по време на изкуствено топлинно и светлинно стареене на хартията.

В този експеримент се използват две лабораторно синтезира реактивни багрила, производни на хлоротриазин като един от тях съдържа стабилизаторен фрагмент. Багрилата се използват в състава на офсетова хартия за печат от избелена целулоза от иглолистна и широколистна дървесина в съотношение 1: 1. Хартията е с проклеяна с алкил кетен димер, а като пълнител е използван природен калциев карбонат. Оптичните свойства - L*, C*, h* на получените проби хартия, от цветовото пространство CIE Lab са определени преди и след изкуствено стареене.

В резултат на проведените изследвания се установи, че с двете реактивни багрила са получени проби хартия с подобни цветови нюанси, еднородно оцветяване и стабилен цвят, отличаващи се със стабилност при топло и светлинно стареене