Bleaching of Paper with the Help of Blue Light Emitting Diodes (LED): Experiments and Results

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ABSTRACT

The authors reviewed the results of experiments on light bleaching of paper objects with the use of blue light emitting diodes (LED) that were carried out and published by them in Russian from 2009 up to 2017. Two light devices with LED emitting blue light at a wave-length of 455–475 nm were used: a spotlight with 180 LED and a special installation with 1200 LED both constructed by Russian LLC “Folga” (St. Petersburg). Paper objects were placed in filtered water containing Ca^{++} and Mg^{++} ions at neutral pH at a distance of 7 cm from the light source, which is considered to be optimal for homogenous illumination. Water-ethanol mixture (1:1) was used as well. The light of chosen wave-length excludes the necessity for UV filters and does not raise the temperature of immersion baths. Objects of different paper composition and age, among them samples with printed and written texts, postcards, engravings and photographs were treated. The treatment’s efficiency was evaluated by changes in paper brightness and paper pH values, as well as by paper appearance before and after treatment. LED radiation for 4 hours was found optimal. The results of artificial humid thermal ageing by indices of brightness, pH, folding endurance of paper and the average degree of cellulose polymerization did not show negative action of the selected bleaching method on the long term stability of chromatographic cotton paper and newsprint paper containing lignin. The method is supposed to be useful in restoration practice.

1 Introduction

The idea of applying blue LED occurred to the authors as a result of studying the light bleaching of paper with fluorescent lamps[1, 2, 3] and in connection with the invention and successful development of LED lighting with its advantages[4]. The authors began with knowledge that short-wave blue light's energy is able to initiate the destruction of chromophores of paper discoloration products, i.e., to bleach paper. So, newsprint paper containing considerable amounts of lignin was bleached at a wave-length between 420 and 510 nm[5,6]. The chemistry of light bleaching can be attributed to the peroxide type, resulting from formation of hydroperoxide ions and radicals in water affected by light and oxygen.

LED emitting light at a wave-length of 455–475 nm was used in our work. The absence of ultraviolet (UV) and infrared rays in this irradiation eliminated the need for an UV light filter and cooling fans for the water bath used, when bleaching paper objects under fluorescent lamps.

Experiments with blue LED have been carried out since 2009 and limited to treatments of objects immersed in aqueous medium. The results of the experiments are described in numerous articles[7, 8, 9, 10, 11]. They are reviewed here in aggregate.

1 Gerasimova et al. (2006), p. 151
2 Gerasimova et al. (2009), p. 28
3 Dobrusina et al. (2011), p. 50
4 Yunovich (2011)
5 Leary (1967), p. 17
6 Feller et al. (1982), p. 65
7 Gerasimova et al. (2011), p. 139
8 Gerasimova et al. (2015), p. 61
9 Gerasimova et al. (2017), p. 268

2 Methods of Treatment and Results Estimation

2.1 Bleaching Devices with Blue LEDs

Initially, a blue SP-S 180-20-220 LED spotlight, provided by St. Petersburg-based LLC “Folga”, was used. The area of illumination is 160 x 120 mm. It contains 180 470-R5-A15 blue LED with a radiation wave-length of 455–475 nm and an illumination angle of 20°. The spotlight power supply voltage is 220 V, with a current consumption of no more than 50 mA and an operational life of at least 100.000 hours (manufacturer data).

The spotlight was suspended upright so that the distance between LED and paper surface was about 7 cm, which is considered optimal for obtaining homogeneous illumination (Fig. 1).

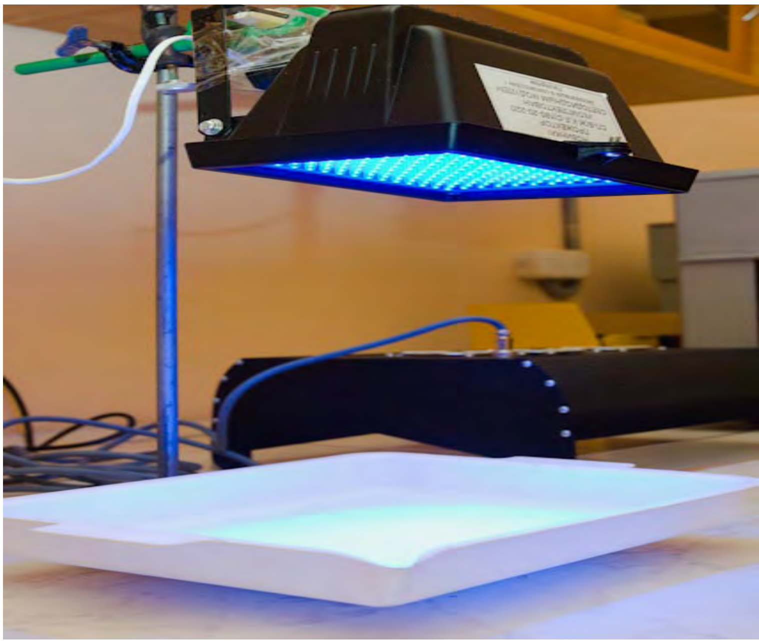


Fig. 1: *Spotlight SP–S 180-20-220 with 180 blue LEDs*

For further research the authors a special LED installation with a maximum area of illumination 300 x 400 mm was designed and constructed in LLC “Folga” according to the authors technical order (Fig. 2). The installation consists of a metal table with legs which height ensuring an optimal distance from the light source to the surface of the samples (7 cm). 1200 blue LED with the same characteristics as in the spotlight are placed on the lower surface of the table plate. The upper surface is supplied with cooling fans. Underneath is placed uncovered plexiglass tray.

Fig. 2: *Installation for light bleaching of paper with 1200 blue LEDs*

2.2 Medium for Bleaching and the Treatment Mode

Water with a neutral pH value was used as a medium for bleaching, specifically tap water filtered through an "Akvafor jug" purifier with an Akvafor V100–1 replaceable filter module produced by LLC "Akvafor"(St. Petersburg), using its own technology. According to the manufacturer, the module provides deep water purification of chlorine, organic impurities, heavy metals. The content of iron ions in filtered water is no more than 0.1 mg/l and no more than 0.001 mg/l of copper ions. Filtered water contains Ca^{++} and Mg^{++} ions, its pH value is within 7.0 – 8.0.

The initial pH value of filtered water in our experiments with blue LED was in the range of 6.8 – 7.6. In part of the experiments, a mixture of filtered water with ethanol in a volume ratio 1:1 was also used as a bleaching medium.

Since the immersed samples were irradiated on one side, they were turned over in the middle of the bleaching period. Various options were considered for the duration of treatment. 4 hours (2 hours on each side) was decided as optimal. In all cases, the treatment began and ended with washing for half an hour in a medium similar to that in which the bleaching was carried out. Thus, the samples passed through three changes of water or water-ethanol. All operations were performed at room temperature.

2.3 Methods of Evaluation of Treatment Results

2.3.1 Physical, chemical and mechanical methods

The results of the treatment were evaluated according to changes in sample brightness, the pH values of their aqueous extracts, and visually through scanning.

Paper brightness was determined by the reflection coefficient of light at a wavelength of 457 nm using an Elrepho 070/071 spectrophotometer, illuminant D65/10°, in accordance with GOST RISO 11475-2010 "Paper and board method for determination of CIE whiteness, D65/10° illuminant (outdoor daylight)". As a rule, measurements were carried out with apertures of 34 or 9 mm, in places without text, images or inscriptions. The results obtained were averaged. Since the method was non-destructive, it could be applied to the same samples before and after treatment or after its definite stage.

The effect of treatment was evaluated by a change of paper brightness $\Delta R = R_t - R_0$, where R_0 and R_t - paper brightness before and after treatment correspondently (%).

The pH value of paper aqueous extract (cold extraction) was determined according to GOST 12523-77 "Cellulose, paper, board method for determination of pH value of aqueous extract" using pH-meters with surface pH electrodes[10].

The influence of treatment on paper mechanical strength was estimated by changes in paper folding endurance measured on a Folding Endurance Tester: at a load of 9.8 N for cotton chromatographic paper and 4.9 N for newsprint paper high in lignin. Before measurements were taken, the samples were preconditioned to 50% RH and a temperature of 18° C in accordance with ISO 5626: 1993 "Paper Determination of Folding Endurance". The change in paper folding endurance as a result of treatment expressed in per cents to the index value before treatment.

For chromatographic paper consisting of pure cotton cellulose, the average degree of cellulose polymerization was determined by measuring the intrinsic viscosity of its solutions in cadoxen[11].

2.3.2 Ageing procedures

The stability of the treatment's effects was estimated by checking the same properties after humid thermal accelerated ageing and light ageing. Humid thermal ageing was carried out at 80° C and 65% RH in a TABAI chamber up to 288 hours.

Light ageing was conducted in the installation with OSRAM DU LUXE 11-860 LUMILUX and PHILIPS PL-L CLEO 3B lamps at 30000 lx illumination at 27° C and the distance 24 cm for 12 hours.

3 The results of the experiments

3.1 Experiments with the blue spotlight

For the first experiments, the following kinds of paper without text were taken:

- rag paper (19th century) made of flax fibers, sized;
- chromatographic paper of M grade (1962) made of cotton fibers without sizing and fillers;
- newsprint paper (1975) made of wood pulp (75%) and unbleached sulfite cellulose (25%);
- paper made of 100% cotton cellulose of experimental production (end of 20th century), hereinafter referred to as cotton paper;
- paper made of 100% sulfite cellulose (end of 20th century), hereinafter referred to as sulfite paper.

4x4 cm paper samples were bleached by the method described above in filtered water irradiated with the blue spotlight for 4 hours, 2 hours on each side. Simultaneously, other samples of the same paper were washed by keeping them in filtered water for 4 hours under ambient light.

Table 1 presents data on the brightness of untreated (control), washed and bleached

10 Mamaeva, Velikova (2016), p. 213
11 Shul´gina (1986), p. 10

samples before and after two types of accelerated ageing: humid thermal for 288 hours and light for 12 hours; Table 2 shows data on the aqueous extract pH of the same samples.

Table 1

Brightness (%) of untreated and treated paper before and after accelerated ageing

Paper	Treatment	Before ageing	Humid thermal ageing 288 h	Light ageing 12 h
Rag	Control	53.0	46.2	56.5
	Washing	55.9	50.8	59.5
	Bleaching	61.6	53.5	63.4
Chromatographic	Control	71.5	56.3	75.3
	Washing	79.7	74.0	82.7
	Bleaching	82.5	76.2	82.2
Newsprint	Control	49.7	39.3	45.9
	Washing	51.8	43.6	47.5
	Bleaching	53.7	42.8	46.6
Cotton	Control	87.6	82.5	87.9
	Washing	88.1	83.7	88.4
	Bleaching	88.6	83.5	88.7
Sulfite	Control	77.9	58.8	76.9
	Washing	80.8	65.4	79.9
	Bleaching	83.9	66.0	80.6

Table 2

Aqueous extract pH value of untreated and treated paper before and after accelerated ageing

Paper	Treatment	Before ageing	Humid thermal ageing 288 h	Light ageing 12 h
Rag	Control	5.7	5.8	5.7
	Washing	6.2	6.3	6.1
	Bleaching	6.4	6.3	6.2
Chromatographic	Control	6.3	6.3	6.3
	Washing	6.8	6.7	6.8
	Bleaching	6.8	6.7	6.8
Newsprint	Control	5.4	5.4	5.1
	Washing	6.5	6.1	5.9
	Bleaching	6.7	6.4	6.0
Cotton	Control	6.6	6.4	6.5
	Washing	6.7	6.4	6.6
	Bleaching	6.7	6.5	6.7
Sulfite	Control	6.0	5.6	5.9
	Washing	6.2	5.8	6.1
	Bleaching	6.5	5.9	6.3

As follows from the data in Table 1 (see "Before ageing"), the effect of brightness increase obtained by washing in filtered water was enhanced by blue irradiation on paper of all kinds. The lowest result was obtained for cotton paper with the highest initial brightness (87.6%): the brightness increase as a result of irradiation was only 0.5%. Light bleaching appeared to be most effective for rag paper with a fairly low initial brightness value (53.0%): the difference in brightness of bleached and washed samples was 5.7%. The brightness of the chromatographic paper after light bleaching increased by 11% (the initial value was 71.5%), the contribution of irradiation being only 2.8%, the rest being the result of washing. Almost the same contribution was made by irradiation in the increase of sulfite paper brightness, but in this case the role of washing was much less. A positive effect was obtained after light bleaching of newsprint paper: its brightness increased by 4% (from 49.7% up to 53.7%), but it was only by 1.9% higher than the result of washing (from 49.7% up to 51.8%).

Humid thermal ageing for 288 hours decreased the brightness of all the tested papers by varying degrees (Table 1), most of all that of untreated sulfite paper, which decreased in brightness by 19.1%. The smallest decrease was seen in cotton paper: 4.4% in the washed sample, 5.1% in untreated and bleached ones. The brightness of untreated chromatographic paper decreased by 15.2%, washed and bleached samples appeared to be significantly more stable, with brightness decreased by 5.6% and 6.3%, respectively. Among the samples of rag paper, the bleached one showed the greatest decrease of brightness (8.1%) and the washed one the least (5.1%). Brightness of untreated newsprint paper after humid thermal ageing decreased by 10.4%, the bleached one by 10.9% and the washed one by 8.2%.

Judging by the index changes in all five types of paper, the washed samples were more resistant to humid thermal ageing than the untreated and bleached ones.

After 12 hours of light ageing, the brightness of all rag paper samples increased: the untreated sample by 3.5%, the washed one by 3.6% and the bleached one by 1.8%; the untreated and washed chromatographic paper samples increased by 3.8 and 3.0%, respectively.

The bleached chromatographic paper sample and all cotton paper samples, which had high brightness values before ageing, were practically unchanged as a result of light ageing. Decrease in brightness was observed in samples of sulfite paper, by 1% in the untreated sample, by 0.9% in the washed one and by 3.3% in the bleached one. Light ageing had the greatest influence on newsprint paper, causing a decrease in the brightness of the bleached sample by 7.1%, that of the washed one by 4.3% and that of the untreated one by 3.8%. It should be noted that at the end of the selected periods of humid thermal and light ageing, bleached samples of all types of paper retained their superiority in brightness over the untreated ones. As Table 2 shows, changes in the paper pH value after the treatments were mainly determined by the influence of filtered water; blue light had little to no effect. In all five kinds of paper which had lower pH in their aqueous extracts than filtered water, the values of the index increased and became closer to neutral.

Both types of accelerated ageing had little effect on the pH values of treated and untreated samples of rag, chromatographic and cotton papers. Sulfite paper showed resistance only to light ageing; after humid thermal ageing, the pH value of the control and washed samples decreased by 0.4 pH units, while that of the bleached one decreased by 0.6. The relatively low pH of untreated newsprint paper (5.4) did not change after humid thermal ageing, but after light ageing decreased by 0.3 units. The pH value of washed and bleached newsprint paper decreased after humid thermal ageing by 0.3 – 0.4 and after light ageing by 0.6 – 0.7 units, but remained 0.7-1.0 pH units higher than that of control samples subjected to similar ageing.

At the next stage, the scope of objects under study was widened, as seen in Table 3. Two bleaching media were compared: filtered water (pH 6.8–7.0) and a mixture of water and ethanol (1:1).

Table 3

Experimental paper material characteristics

№	Paper, dating	Fiber composition	Sizing	Thickness, mm	Text material	Note
1	strong rag paper, 19th century	flax, hemp	gelatin	0.28	without text	light brown stains (tide lines)
2	loose rag paper, 19th century	flax	gelatin	0.29	without text	Reddish foxing
3	grey rag paper, 19th century	flax	starch, gelatin	0.15	without text	brownish foxing
4	rag paper, 1852	flax	gelatin	0.13	iron gall ink	yellowness
4a	the same	flax	gelatin	0.13	black printing ink	the same
5	rag paper 19th century	flax	gelatin	0.13	campesian ink, red-brown pencil	the same
6	chromato-graphic paper, 1962	cotton	-	0.16	without text	the same
7	newsprint paper, 1975	bleached wood pulp — 75%, sulfite cellulose — 25%	-	0.09	without text	the same
8	book paper, 1915	wood pulp — 70%, softwood cellulose — 15%, flax — 15%	gelatin	0.09	black printing, campesian ink	the same
9	newsprint paper, 1954	wood pulp — 70%, softwood cellulose — 30%	-	0.10	black printing ink	the same

The experiments were carried out with 4 x 4 cm samples. Side views of the samples are shown in Figures 3 and 4, where the first sample in each row was not treated (control), the second one was washed in water, the third one was bleached in water, the fourth one was bleached in a mixture of equal volumes of water and ethanol. Bleaching and washing methods were the same as described previously. In this case brightness was measured all over sample surface for both sides of each sample before and after treatment. The brightness values obtained for the samples side shown in Figures 3 and 4 are given in Table 4.

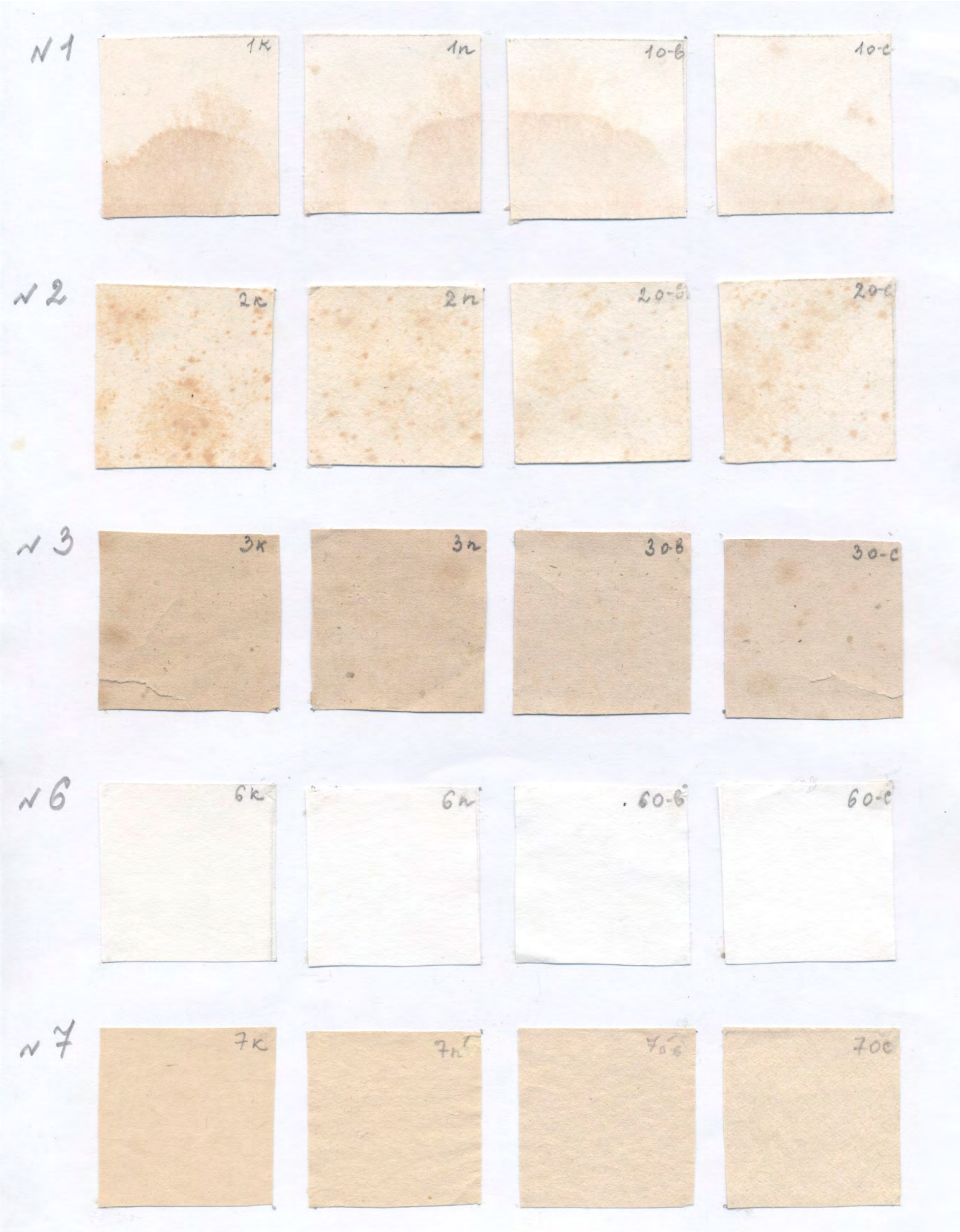


***Fig. 3:** Samples without text: column 1 – control, 2 – washed, 3 – bleached in filtered water, 4 – bleached in water-ethanol mixture*

***Fig. 4:** Samples with text: column 1 – control, 2 – washed, 3 – bleached in filtered water, 4 – bleached in water-ethanol mixture*

Brightness increase (ΔR_{457}) after treatment (washing or bleaching) was calculated for each side and averaged for the whole sample. In Table 5, average values of ΔR_{457} for washed and bleached samples are presented. The data on pH of samples aqueous extracts are shown in Table 6.

These experiments confirmed earlier findings on the effectiveness of blue LED for light bleaching of various papers and the neutralizing action of filtered water. Comparison of brightness increase (Table 5) after bleaching in water and water–ethanol mixture showed the advantage of the latter for seven kinds of samples out of ten, including all kinds of paper containing wood pulp (№ № 7 – 9).

Table 4

The samples brightness (%) on the side represented in Figures 3 and 4 (for № meaning see Table 3)

№	Control	Washing	Bleaching in water	Bleaching in water – ethanol
1	59.0	67.0	67.2	71.1
2	52.3	56.0	69.5	61.4
3	38.0	40.4	45.7	46.0
4	44.2	46.3	50.4	54.9
4a	46.5	46.7	50.9	55.9
5	51.2	55.0	54.5	57.3
6	81.5	85.4	87.2	87.2
7	47.9	49.2	52.5	54.9
8	36.3	39.8	41.5	43.1
9	34.6	35.0	37.3	40.0

Table 5

The samples brightness increase (ΔR457 , %) as the result of treatments (for № meaning see Table 3)

№	Washing	Bleaching in water	Bleaching in water – ethanol
1	5.9	8.7	11.0
2	3.3	12.0	9.3
3	2.5	7.7	8.5
4	1.9	5.5	9.6
4a	1.8	6.0	8.8
5	1.1	1.0	1.0
6	2.8	4.1	4.1
7	1.5	5.0	6.6
8	3.3	4.1	7.4
9	0.2	3.2	5.9

Table 6

pH of paper samples before and after treatments (for № meaning see Table 3)

№	Control	Washing	Bleaching in water	Bleaching in water – ethanol
1	6.1	6.5	6.6	6.5
2	6.0	6.6	6.6	6.6
3	6.3	6.6	6.7	6.6
4	5.2	6.5	6.5	6.4
4a	5.1	6.3	6.3	6.3
5	4.9	6.4	6.4	6.3
6	6.0	6.6	6.6	6.5
7	5.0	6.5	6.5	6.4
8	5.5	6.5	6.6	6.6
9	5.0	6.3	6.3	6.3

The experiments made it possible also to draw some conclusions about the influence of the treatments on certain writing and printing materials.

Judging by the visual observation, (Figure 4) the colour intensity of iron gall ink and black printing ink on rag paper (samples №№ 4 and 4A) did not change after water treatments and faded only slightly after water-ethanol treatments. None of the treatment types affected the campesian ink or red–brown pencil on rag paper (sample № 5). The campesian ink on 1915 book paper (sample № 8) did not change after treatments, while printed text on the same sample got noticeably diffused after water treatments and did not change after water-ethanol bleaching. The printed text of a 1954 newspaper (sample № 9) got partially diffused after all treatments.

The results showed the need for further studies on larger samples and documents. In this regard, a special LED installation was made.

3.2 Experiments with LED Installation

The effectiveness, influence on the properties of paper and potential practical use in restoration of bleaching using LED installation was examined. The objects of the study were samples of chromatographic and newsprint paper, (Table 3, №№ 6 and 7) as well as some printed materials and photographs (Table 8).

Table 7

Indices values of untreated and bleached paper properties before and after humid thermal ageing for 216 hours

Paper	Brightness, %	N, double folds	pH	DP
Chromotographic: Untreated	81.8	54	6.0	883
Untreated, aged	74.2	37	5.9	872
Bleached	86.8	51	6.5	892
Bleached, aged	82.8	38	6.3	872
Newsprint: Untreated	50.0	125	5.3	-
Untreated, aged	39.8	54	5.1	-
Bleached	54.0	220	6.0	-
Bleached, aged	46.5	96	5.5	-

Table 8

Data on the document bleached in the LED installation

№	Name/type of a document	Size, mm	Fiber composition of paper	Notes
1	Engraving A Bookplate “Shield”	230x146x0.16	flax	Yellowing, tidelines
2	Engraving B Bookplate “Eagle”	245x157x0.13	flax	Yellowing, stains
3	Leaflet "Alisher Navoi", Tashkent, 1941	297x209x0.15	wood cellulose	Yellowing, localized yellow stains
4	«Builder Solness» - scene from V.F. Komissarzhevskaya theatre play – Postcard, Moscow, 1905	87x137x0.32	wood cellulose with admixture of textile fibers (~2%)	Slight yellowing
5	V.F. Komissarzhevskaya portrait. Postcard, Moscow, 1922	136x85x0.23	wood cellulose	Significant yellowing, separate yellow stains
6	A portrait of a woman. Photograph, Leningrad, near 1940	191x131x0.26	wood cellulose	Yellowing, tidelines, the sheet corrugation remains of wood pulp carboard mounting
7	A carpet fragment. Photograph, Leningrad, 1937-1939	151x236x0.17	wood cellulose	Yellowing, yellow stains. Violet stamp, violet ballpoint pen ink

3.2.1 Effect of Treatment on Paper Properties

Samples of chromatographic and newsprint paper were immersed in filtered water (pH 7.1) and irradiated in the LED installation for 4 h (2 h on each side) being washed in filtered water for 30 min before and after irradiation. Half of the untreated and bleached samples were subjected to humid thermal ageing for 216 hours. The values of brightness, folding endurance (N, double folds) and pH of paper aqueous extract of all samples were determined. For the samples of chromatographic paper consisting of cotton cellulose without sizing agents and fillers, the average degree of cellulose polymerization (DP) was also determined. The results are given in Table 7.

As Table 7 shows, the brightness of chromatographic paper increased after bleaching by 5% and reached 86.8%. Humid thermal ageing reduced the brightness of untreated paper by 7.6% and that of bleached paper by only 4%.

Bleaching did little to change chromatographic paper folding endurance, its decrease was within the measurement error. After ageing, both unbleached and bleached samples had approximately equal folding endurances, which was less than 25–30% for those before ageing. The pH value of the aqueous extract of chromatographic paper rose as a result of bleaching from 6.0 to 6.5. Humid thermal ageing increased the acidity of its untreated and treated samples slightly, by 0.1–0.2 pH units. Bleaching did not affect the average degree of polymerization of chromatographic paper cellulose or its resistance to humid thermal ageing. After ageing, the degree of polymerization of untreated and bleached paper was the same, which was in accordance with the values of their folding endurance.

As for newsprint paper, its brightness increased by 4% and reached 54%. Accelerated ageing reduced the brightness of untreated paper by 10.2% and bleached paper by only 7.5%. Bleaching significantly increased the folding endurance of newsprint paper. After accelerated ageing, bleached and unbleached samples showed the same decrease of the folding endurance, i.e., even after ageing bleached paper retained its superiority in strength over unbleached paper. The pH value of the newsprint paper aqueous extract after bleaching increased by 0.7 pH units, reaching 6.0, and after ageing it was 0.4 pH units higher than that of untreated paper.

Thus, bleaching with blue light in the LED installation increased the brightness and reduced the acidity of both cotton fiber paper (chromatographic) and paper with a high content of lignin (newsprint paper). The degree of polymerization and folding endurance of chromatographic paper did not change, while the strength of newsprint paper increased significantly. After humid thermal ageing for 216 hours, the bleached samples of both papers retained superiority over unbleached ones in terms of brightness, pH values, and in the case of newsprint paper, folding endurance. Besides, the bleached paper showed better stability of brightness under humid thermal ageing.

3.2.2 Experimental Bleaching of Documents

Information on the documents bleached in the LED installation is given in Table 8. These are engravings, printed editions with text, postcards and photographs, dated from 1901-1941, all of which are the property of the authors. Bleaching was intended to improve the appearance of the objects and to check the changes. The appearance was recorded by scanning before treatment and after each stage. Brightness and pH were measured.

Two engravings printed on paper made of flax fiber with a weak gelatin sizing (Table 8, №№ 1 and 2, Fig. 5) were bleached first.

After pre-washing for 30 min, the engravings were bleached 6 times in filtered water. Each of the six bleaching procedures was carried out for 4 hours (2 hours on each side of the engraving), followed by washing in fresh filtered water and drying between sheets of filter paper for two days and nights. Brightness was measured before the treatment and after each stage in the five areas selected on the reverse side of the engraving, the results being averaged (Table 9).

Table 9

Brightness of the engravings paper before and after the treatment stages

Treatment	Brightness, %	
	Engraving A	Engraving B
Before treatment	38.9	54.4
Pre-washing (30 min)	42.2	59.1
Bleaching duration, hour:		
4	51.6	69.5
8	55.8	73.1
12	59.2	74.6
16	62.2	76.0
20	63.1	76.6
24	64.5	77.3

Fig. 5: *Engravings A and B before and after treatments*

Washing in filtered water for half an hour increased the brightness of the paper support of engraving A by 3.3% and that of engraving B by 4.7%. Bleaching for 4 hours led to an increase in the brightness of engraving A by 9.4% and for engraving B by 10.4% when compared with pre-washing levels. With further exposure to light up to 24 hours, the brightness continued to increase while gradually slowing down.

Figure 5 represent the appearance of the engravings A and B, recorded by scanning, before treatment, after washing and after bleaching for 4 hours and for 24 hours.
The influence of the treatment on the engravings printing ink was not noticed.

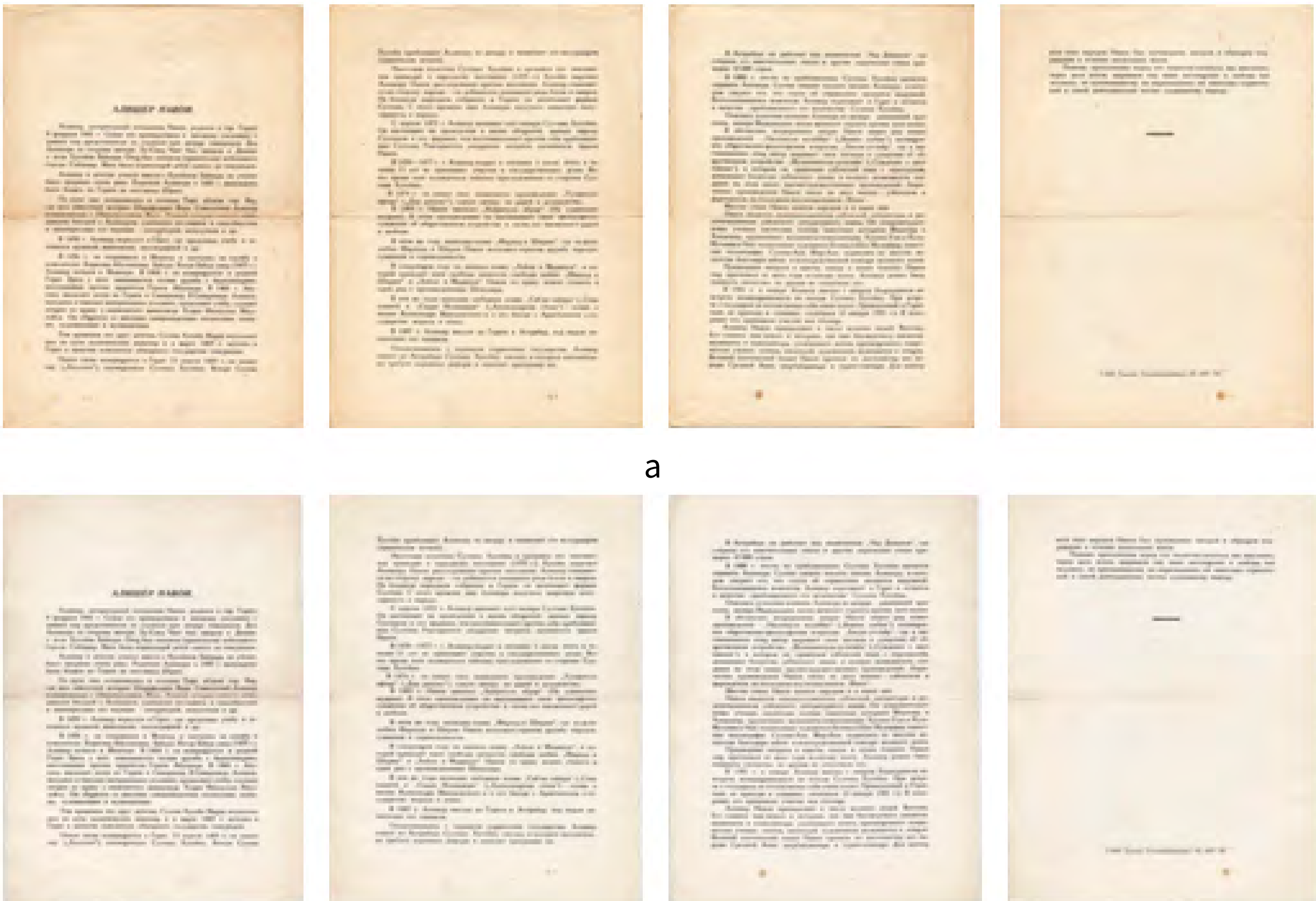
Sheets of printed publications (Table 8, № 3, Fig. 6) and postcards (Table 8, №№ 4 and 5, Fig. 7 and 8) were treated in a similar manner. The only difference was the duration of LED bleaching, which was limited to 4 hours.

The obtained data on paper brightness and pH values of the objects paper of this group are shown in Table 10.

Table 10
The effect of bleaching treatment on the paper brightness and pH value of the paper aqueous extract

Object №	Brightness, %		pH	
	Before treatment	After treatment	Before treatment	After treatment
3	49.5*	59.0*	4.5*	5.2*
4	50.0	55.5	5.0	5.7
5	30.0	45.5	4.2	5.0

Note: * average value for two sheets.



a

b

Fig. 6: *Leflet "Alisher Navoi": a – before treatment, b – after bleaching (4 h)*

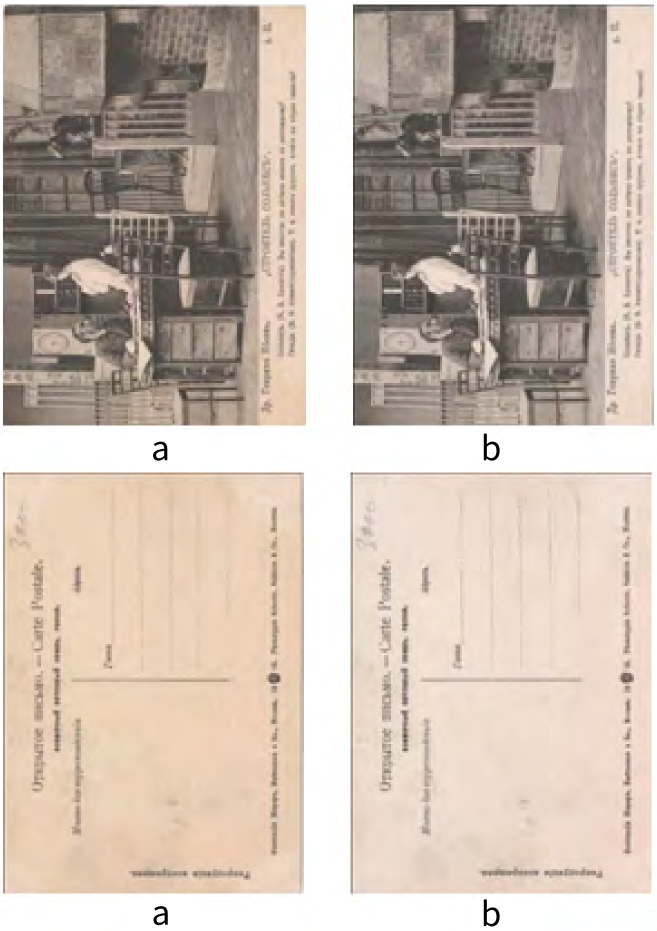


Fig. 7: *Postcard "Builder Solness" – a scene from the performance of the V. F. Komissarzhevskaya theater: a – before treatment, b – after bleaching (4 h)*

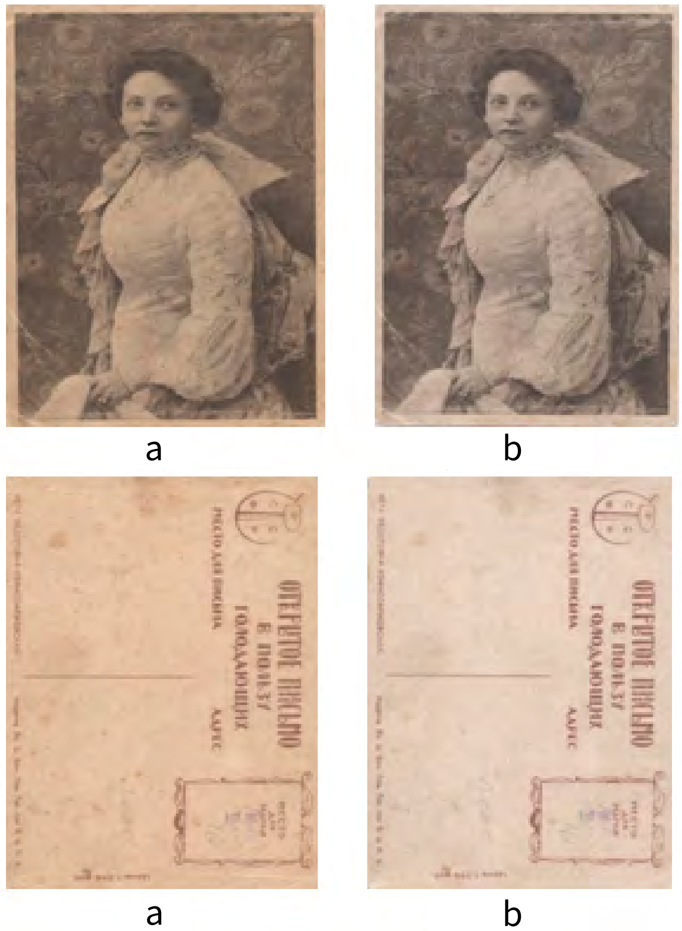


Fig. 8: *Postcard "Portrait of V. F. Komissarzhevskaya»: a – before treatment, b – after bleaching (4 h)*

"Alisher Navoi" (№ 3) leaflet pages, before and after treatment, are presented in Figure 6. The treatment resulted in yellowness removal, the increase in brightness was about 10%, printing ink was well preserved.

The increase in paper brightness of a postcard with a scene from the play "Builder Solness" (№ 4), which had no significant yellowness and stains, was small (5.5%), but the result obtained was quite satisfactory (Fig. 7). On the contrary, the brightness of the postcard paper with a portrait of V. F. Komissarzhevskaya (№ 5), strongly yellowed and with numerous stains, increased significantly after bleaching (by 15.5 %). The appearance of the card improved and the print was not affected (Figure 8).

The paper of all four objects of this group had high acidity, ranging from 4.2 (№ 3) to 5.0 (№ 4). As a result of treatment in all cases, a decrease in acidity (an increase in the pH value) by 0.7 – 0.8 pH units was achieved.

Work with this group of objects confirmed the effectiveness of the applied mode of LED bleaching as a way to increase paper brightness and reduce its acidity, without affecting texts and images made with printing ink and graphite pencil.

The photographs (Table 8, №№ 6, 7) were treated in the same manner, the only difference being that when drying in a press between sheets of filter paper, the photo was covered with a sheet material of Parafil KT 30 on the face side to prevent the adhesion of the wet photo layer to the filter paper.

The woman's portrait (Fig. 9), which had background yellowing, sheet deformation, tide line and significant discolouration in the lower part with cardboard remains from the mounting, had been bleached for 4 hours (similar to objects № 3 – 5). The brightness values of the face and reverse sides of the photograph before treatment, after washing and after bleaching are given in Table 11.

***Fig. 9:** A woman portrait. Photograph:*
a – before treatment, b – after washing (0.5 h),
c – after bleaching (4 h)

Table 11
The effect of bleaching treatment on the paper brightness and pH value of the paper aqueous extract

Object №	Brightness, %		pH	
	Before treatment	After treatment	Before treatment	After treatment
3	49.5*	59.0*	4.5*	5.2*
4	50.0	55.5	5.0	5.7
5	30.0	45.5	4.2	5.0

Note: * average value for two sheets.

The treatment resulted in a brightness increase on the face side by 9% and that of the reverse side by 9.5%. The discolouration and the tide line were significantly diminished. The deformation was eliminated in the process of drying in a press; the photo image remained unchanged.

The photograph of a carpet fragment (Fig. 10) had slight yellowing of the paper, a large yellow stain and small stains on the reverse side, which were almost not reflected in the image on the face side. This photo was bleached in two stages, 30 min each, with the face and reverse sides being irradiated for 15 min at each stage. Data on the brightness values of the reverse side measured before and after treatment are shown in Table 12. In this case, a satisfactory result was achieved as soon as half an hour after bleaching with preliminary washing. Paper brightness increased by 6.5% and in the area of the stain by 9%. The next 30 min of bleaching led to a further increase in brightness, but only by 1 – 1.5%. The photo image remained well preserved.

The experiments with black-and-white photographs showed the possibility of using the LED installation for bleaching the paper

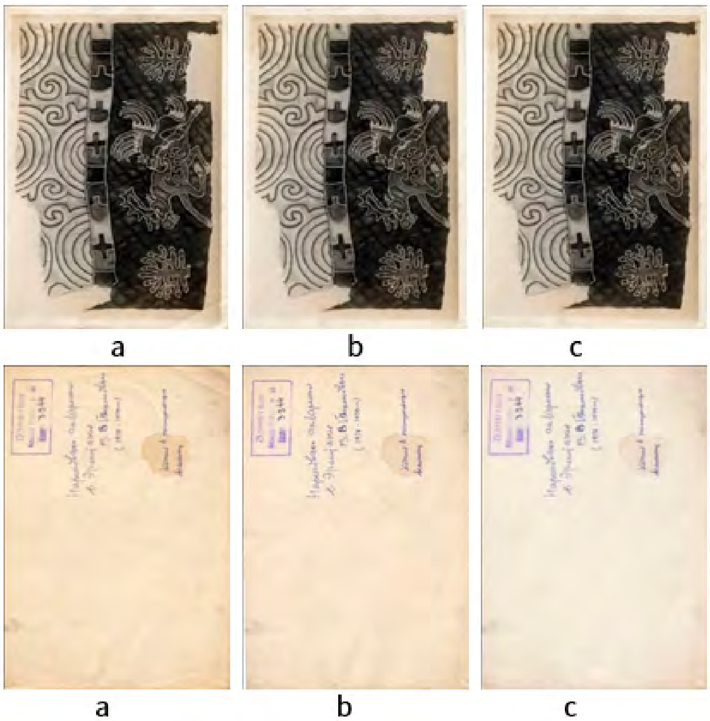


***Fig. 10:** Photograph of a carpet fragment:*
a – before treatment, b – after washing (30 min),
c – after bleaching (60 min)

Table 12
The effect of bleaching treatment on the paper brightness and pH value of the paper aqueous extract

Treatment type	Treatment duration, min	Brightness, %	
		Area without stain	Area with stain
Before treatment		48.5	37.0
Washing	30	51.5	42.0
Bleaching:			
1 stage	30	55.0	46.0
2 stage	30	56.0	47.5

support of such objects without affecting the photo image. The presence of inscriptions with a ballpoint pen and a stamp on the reverse side of one of the photos (Fig. 10) made it possible to note the stability of violet ball point ink during pre-washing and light bleaching for 60 minutes and the blurring of violet stamp ink around its contours, which occurred in the very process of pre-washing.

4 Conclusion

It was experimentally shown that light bleaching of paper objects through irradiation with a wave-length of 455–475 nm obtained from blue 470–R5–A15 LEDs could be used. For the experiments, a lighting device (spotlight) with an illuminating area of 160 x 120 mm, containing 180 LEDs, and a specially designed installation with 1200 LEDs with a maximum illuminating area of 300 x 400 mm were used. The absence of UV and IR rays in the irradiation allows the process to be carried out at room temperature and without UV filters.

Irradiation for 4 hours (2 hours on each side of the object) in tap water, purified by an "Akvafor Jug" filter, with pre- and post-washing for 30 min, was chosen as an optimum mode. Filtered water with pH 7–8, containing ions Ca^{2+} and Mg^{2+}, gives paper a neutralizing effect and increases paper resistance to ageing. In some experiments, a mixture of this water and ethanol (1:1) was used.

The efficiency of the chosen method was shown on various papers made of flax, cotton, sulfite cellulose, wood pulp, as well as on samples and separate sheets with printed and handwritten texts, engravings, postcards and black-and-white photographs. The treatment efficiency was evaluated mainly by increases in paper brightness and pH values. Comparison of two bleaching media, water and water-ethanol mixture (1:1), showed the greater efficiency of the latter in most cases.

The results of humid thermal ageing by indices of brightness, pH, folding endurance of paper and the average degree of cellulose polymerization indicated the absence of negative influence of the selected method of bleaching on the durability of chromatographic paper made of cotton fibers and newsprint paper with high content of lignin.

Observations on the behavior of some printing and writing materials in the washing and bleaching processes showed that campesian ink, graphite and color (red–brown) pencils withstood water and water-ethanol mediums. Black printer's ink and iron gall ink on rag paper did not change after treatments in water and slightly faded after bleaching in water- ethanol mixture, while printed text on 20th century newspaper showed a tendency to diffuse in both mediums. After water treatments violet stamp ink diffused a little around the stamp contour and violet ballpoint pen paste did not change.

The results of the experiments suggest that the proposed method of paper bleaching with blue LED will probably find its place in restoration practice.

References

Gerasimova et al. (2006)
Герасимова Нина Г., Добрусина Светлана А., Вовк Наталья С.: Исследование процесса светового отбеливания бумаги в установке «Пультекс» с люминесцентными лампами, Обеспечение сохранности памятников культуры: традиционный подход — нетрадиционные решения, материалы V Международной конференции, 24-26 октября 2006 г., Российская национальная библиотека (РНБ), Санкт-Петербург, 2006, с. 151–166. (Gerasimova, Nina G., Dobrusina, Svetlana A., Vovk, Natalya S.: Study of the process of light bleaching of paper in the installation "Pultex" with fluorescent lamps. In: Ensuring the preservation of cultural monuments: traditional approach-unconventional solutions. Materials of the Vth International Conference, 24–26 October 2006, National Library of Russia (NLR), St. Petersburg, NLR, (2006), pp. 151–166).

Gerasimova et al. (2009)
Герасимова Нина Г., Добрусина Светлана А., Вовк Наталья С.: Изучение зависимости эффективности светового отбеливания от композиции бумаги, Теория и практика сохранения памятников культуры, сборник научных трудов, РНБ, Санкт-Петербург, 2009, вып. 22, с. 28–38. (Gerasimova, Nina. G., Dobrusina, Svetlana A., Vovk, Natalia S.: Study of the dependence of light bleaching efficiency on paper composition. In: Theory and practice of cultural monuments preservation, vol. 22, St. Petersburg, NLR, (2009), pp. 28-38).

Gerasimova et al. (2011)
Герасимова Нина Г., Добрусина Светлана А., Волгушкина Наталья С., Цитович Вероника М.: Отбеливание бумаги с использованием светодиодных ламп, Труды ЛКРД Санкт-Петербургского филиала Архива РАН, вып. II, Актуальные проблемы сохранения архивных, библиотечных и музейных фондов, Санкт-Петербург, Реликвия (реставрация, консервация, музеи), 2011, с. 139-154. (Gerasimova, Nina G., Dobrusina, Svetlana A., Volgushkina, Natalia S., Tzitovich, Veronika M.: Paper bleaching using LED lamps. In: Proceedings/Laboratory of documents conservation and restoration, St. Petersburg branch of the Archive of the Russian Academy of Sciences, vol. II, Actual problems of archival, library and museum funds preservation, St. Petersburg, Relicvya (restoration, conservation, museums), (2011), pp. 139–154).

Gerasimova et al. (2015)
Герасимова Нина Г., Добрусина Светлана А., Волгушкина Наталья С., Цитович Вероника М.: Отбеливание бумаги документов в экспериментальных установках с синими светодиодами, Теория и практика сохранения памятников культуры, сборник научных трудов, РНБ, Санкт-Петербург, 2015, вып. 24, с. 61–71. (Gerasimova, Nina G., Dobrusina, Svetlana A., Volgushkina, Natalia S., Tzitovich, Veronika M.: Bleaching of paper documents in experimental installations with blue LEDs In: Theory and practice of cultural monuments preservation, vol. 24, St. Petersburg, NLR, (2015), pp. 61–71).

Gerasimova et al. (2017)
Герасимова Нина Г., Добрусина Светлана

А., Волгушкина Наталья С. Оценка свойств бумаги в процессе отбеливания синим светом в светодиодной установке, Теория и практика сохранения памятников культуры, сборник научных трудов, РНБ, Санкт-Петербург, 2017, вып. 25, с. 268–273. (Gerasimova, Nina G., Dobrusina, Svetlana A., Volgushkina, Natalia S. Evaluation of paper properties in the process of bleaching with blue light in LED installation In: Theory and practice of cultural monuments preservation, vol. 25, St. Petersburg, NLR, (2017), pp. 268–273).

Gerasimova et al. (2017)
Герасимова Нина. Г, Добрусина Светлана А., Волгушкина Наталья С.: Опыт применения светодиодной установки для отбеливания некоторых печатных материалов и фотографий, Теория и практика сохранения памятников культуры, сборник научных трудов, РНБ, Санкт-Петербург, 2017, вып. 25, с. 274–281.Gerasimova, Nina G., Dobrusina, Svetlana A., Volgushkina, Natalia S.: Experience of LED installation application for bleaching of some printed materials and photos. In: Theory and practice of cultural monuments preservation, vol. 25, St. Petersburg, NLR, (2017), pp. 274-281).

Gerasimova et al. (2017)
Герасимова Нина Г., Добрусина Светлана А., Цитович Вероника М.: Об эффективности отбеливания бумаги синим светодиодным прожектором и влиянии обработки на материалы письма и печати, Лики памяти, статьи VII Международной научно-практического семинара, Ереван, Армав, 2017, с. 128–138. (Gerasimova, Nina G., Dobrusina, Svetlana A., Tzitovich, Veronika M.: On the effectiveness of paper bleaching with a blue LED spotlight and the influence of treatment on writing and printing materials. In: Liki pamiaty (Faces of the memory), 7 International Scientific and Applied Workshop, Erevan, Armav, Matenadaran, (2017), pp. 128–138).

Dobrusina et al. (2011)
Добрусина Светлана А., Волгушкина Наталья С., Герасимова Нина Г.: Влияние светового отбеливания на акварельные краски при реставрации произведений графики, Оптический журнал, 2011, т. 78, вып. 10, с. 50–57. (Dobrusina, Svetlana A., Volgushkina, Natalia S., Gerasimova, Nina G.: Influence of light bleaching on watercolor paints during graphic works restoration. In: Opticheskiy Zhurnal (Journal of Optical Technology) 78, 10 (2011): pp. 50–57).

Feller et al. (1982)
Feller, R. L., Lee, S. B., Bogaard, J.: The Darkening and Bleaching of Paper by Various Wavelengths in the Visible and Ultraviolet. The AIC Book and Paper Group Annual, 1 (1982),
pp. 65–81.

Leary (1967)
Leary, G. L.: The Yellowing of Wood by Light. TAPPI, 50, (1967), pp. 17–19.

Mamaeva, Velikova (2016)
Мамаева Наталья Ю., Великова Татьяна Д.: Инструкция по измерению pH бумаги контактным методом, Лабораторные методики и технологические инструкции в консервации документов, РНБ, Санкт-Петербург, 2016, с. 213–220. (Mamaeva, Natalia Yu., Velikova, Tatʾyana

D.: Instructions on measuring the pH of paper by contact method. In: Laboratory methods and technological instructions in documents preservation, St. Petersburg, NLR, (2016), pp. 213–220).

Shul´gina (1986)
Шульгина Э. С.: Характеристическая вязкость и размеры молекулярных клубков в растворе, Свойства растворов полимеров: методические указания, ЛТИ, Ленинград, 1986, с. 10–17. (Shulgina, E. S.: Intrinsic viscosity and size of molecular coils in a solution. In: Polymers solutions properties: method, instructions, Leningrad, Leningrad Technological Institute, (1986) pp. 10–17).

Yunovich (2011)
Юнович А.Э.: Светодиоды и их применение для освещения, под редакцией Ю.Б. Айзенберга, Москва, Знак, 2011, 16 с. (Yunovich, A. E.: Light-emitting diodes and their application for lighting. Moscow, Znak, (2011), 16 p.).

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