Ayhan Gençer[1], Cengiz Keşmer*[2], Ayben Kılıç Pekgözlü[1], Mehmet Bebekli[3], Ahmet Can[1], Esra Ceylan[1]

Using Dyestuff Obtained from Turkish Red Pine Bark Combined with Cationic Starch in Paper Dyeing

Upotreba bojila dobivenog iz kore turskoga crvenog bora u kombinaciji s kationskim škrobom za bojenje papira

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ABSTRACT • *This study will be important in reducing water pollution, especially by not using chemical agents in the dyeing process and using organic mordant in the paper dyeing process. The cationic starch (CS) is also used as a mordant. CS increases the dry strength properties of the paper as well as the dye adhesion, and it is important in terms of providing two functions to an additive at the same time. In this study, natural dyestuff was obtained from Turkish red pine (Pinus brutia Ten.) bark by boiling in water, and bleached eucalyptus pulp was dyed. CS, which can increase the paper dry strength, was used as a mordant in the dyeing process. CS was mixed with distilled water in a hot water bath at (95±2) ºC and gelled. Thanks to 1.5 % CS addition, the tensile index increased by 38 %. With the addition of dyestuff, the papers became red and yellow. Adding CS and increasing the amount of dyestuff darkened the tone of these colors. However, CS addition was more effective than increasing the amount of dyestuff. That is to say, increasing the amount of dye alone in CS-free papers was not as effective as in CS-added papers.*

KEYWORDS: *Turkish red pine bark; organic dyestuff; starch; mordant; UV-ΔL*

SAŽETAK • *Rezultati ove studije važni su za smanjenje onečišćenja vode, posebice zato što se u procesu bojenja papira ne rabe kemijska sredstva, kao i zato što se pritom kao organski fiksator upotrebljava kationski škrob (CS). On povećava svojstva čvrstoće suhog papira, kao i fiksiranje bojila, a važan je u smislu ostvarivanja dviju funkciju aditiva istodobno. U ovom je istraživanju prirodno bojilo dobiveno iz kore turskoga crvenog bora (Pinus brutia Ten.) kuhanjem u vodi, a njime je obojena izbijeljena pulpa eukaliptusa. Kationski škrob, koji može povećati čvrstoću suhog papira, poslužio je kao fiksator u procesu bojenja. Kationski je škrob pomiješan s destiliranom vodom u vrućoj vodenoj kupelji na (95 ± 2) ºC i želiran. Zahvaljujući dodatku 1,5 % kationskog škroba, vlačni indeks papira povećao se za 38 %. Nakon dodanog bojila papiri su postali crveni i žuti, a uz dodatak kationskog škroba i s povećanjem količine bojila ton boje postao je tamniji. Međutim, dodavanje kationskog škroba bilo je učinkovitije od povećanja količine bojila, tj. pokazalo se da povećanje količine bojila u papirima bez kationskog škroba nije dalo tako dobre rezultate kao u papirima s dodatkom kationskog škroba.*

KLJUČNE RIJEČI: *kora turskoga crvenog bora; organsko bojilo; škrob; fiksator; UV-ΔL*

* Corresponding author
[1] Authors are researchers at Bartin University, Faculty of Forestry, Department of Forest Industrial Engineering, Bartin, Türkiye.
[2] Author is researcher at Çukurova University, Aladağ Vocational High School Forestry Department, Adana, Türkiye.
[3] Author is researcher at Çukurova University, Faculty of Engineering, Department of Textile Engineering, Adana, Türkiye.

1 INTRODUCTION
1. UVOD

The substances found in nature are in different colors because their structures refract light at different angles. Many materials are used for recoloring for various reasons. The process of converting one color to another is done with dye or dyestuff. Dyestuffs are grouped into two main groups: natural and synthetic origin. Natural dyestuffs are obtained from plants, animals, and minerals. Natural dyestuffs obtained from plants and animals are renewable and therefore sustainable.

Dye is applied to a surface with a binder that can dry out, with brushes or spray guns. It can be removed from the applied surface by scraping. Dye is a colored substance that chemically bonds to the substrate to which it is applied (Devi, 2014). Dyestuff, on the other hand, is the substance used in the coloring of objects (fabric, fiber, etc.), and it cannot be removed by scraping (Önal, 2000).

Cellulose is known for its low affinity for anionic entities and therefore cannot form strong bonds with most natural dyes without mordant. The fact that the mordant used is cationic improves the aforementioned negative properties (Bechtold and Mussak, 2009).

The use of mordant in dyeing textile products with natural dyestuffs is common, with aluminum and iron salts, acids, and various minerals being preferred. By obtaining dyestuff from onion skin (*Allium cepa* L.) and using various metal salts as a mordant, high-fastness dyeing of hairy leather and cotton fabric has been carried out (Eser and Önal, 2010). Wool fabric was dyed with the dyestuff obtained from red pine bark. It has been stated that light, washing, and rubbing fastness are at the desired level and in usable condition (Akpınarlı and Yalçın, 2012). It has been emphasized that cotton fabrics are dyed in the presence of metal salts as a mordant with the dyestuff obtained by ethanol extraction from the pomegranate peel, and the colorfastness, washing fastness, and friction fastness of these fabrics are satisfactory. They also stated that this dyestuff can be used instead of banned arylamine dyes (Kulkarni *et al.,* 2011). Metal salts, aloe vera, and lemon juice were used as mordants in dyeing the cotton with dyestuff obtained from onion skin extract. It was stated that the best color yield was obtained with lemon juice mordant (Zubairu and Mshelia, 2015). Organic cotton fabrics were dyed with dyestuff from madder root, walnut shell, henna, horse chestnut, pomegranate peel, berberis vulgaris root, thyme, and sage tea. The color and fastness properties obtained from the dyed organic cotton fabrics were between good to excellent (Tutak and Korkmaz, 2012). In a study, the effect of different amounts of metals on the coloring scale of the pigments was investigated. For this purpose, the reaction of the dyestuffs present in buckthorn with aluminum(III), iron(II), and tin(II) was used to prepare natural pigments (Deveoglu *et al*., 2009). Natural yellow pigments from the hemp (*D. cannabina L.*) dye plant were prepared by using KAl $(SO_4)_2 \cdot 12H_2O$ (alum), $FeSO_4 \cdot 7H_2O$ and $SnCl_2 \cdot 2H_2O$ mordants (Deveoglu *et al.,* 2012). It has been reported that alum mordant is more suitable to accompany Turkish red pine bark extract in natural extract dyeing with one exception (flax); however, the use of oak ash natural mordant is beneficial when completely eco-friendly dyeing is desired (Avinc *et al.,* 2013). The enzymatic dyeing of Ferrulic Acid provides fabrics with multifunctional properties of antioxidant activity, UV protection, and deodorization (Sun *et al.,* 2015). A study used *Pistacia vera* hulls by-product extract as a dyestuff. Dyed samples exhibited good fastness to washing, rubbing, and light (Syrine *et al.,* 2020).

Onion peel, henna, pomegranate, pomegranate peel, and rose petals were extracted to produce natural dyestuffs. Alum was used as a mordant in dyeing the paper by dipping the paper into the dyestuff. Henna-dyed samples showed the highest color stability after aging in dyed papers, while pomegranate-dyed samples showed the least color stability (Çakar, 2012). A study extracted the dyestuff from eucalyptus bark with distilled water at different temperatures and stated that the dyestuff they obtained at the boiling temperature provided the best relative color strength in cotton dyeing (Ali *et al*., 2006).

In a study, dyestuff obtained from elderberry (*Sambucus nigra*) plants seeds used paper pulp dyeing by using alum as a mordant. It has been reported that dyestuff adhesion in papers obtained from pulps without mordant additions is weaker than in those with mordant additions (Gençer and Can, 2016). Wild cherry (*Cerasus avium* L.) tree bark extract is used as a dyestuff in paper production (Gençer *et al.,* 2019a). It has been stated that the UV resistance of the papers using alum as a mordant is high. The dyestuff obtained from the bark of wild cranberry (*Cornus australis* L.) was used to dye the pulp obtained from the mixture of waste papers of various origins. It has been reported that color homogeneity is achieved in the papers obtained from the mixture (Gençer *et al.,* 2019b). In a study to determine the dyestuffs used in manuscripts of the 15th century, non-destructive analyses were carried out with μXRF, Raman, and FTIR spectroscopy. Samples were taken from the fragments of these artifacts, and chromatographic analyses were performed. It was concluded that these papers were colored with Isgin (*Rheum ribes* L.) based on the compounds detected (Çakar, 2019).

Cellulose and hemicelluloses contain hydroxyl and carboxyl groups. They carry a negative charge due to the carbonyl and carboxyl groups formed by the bleaching process (Eroğlu, 1989). Cationic groups in cationic starches have a positive charge effect on starch; showing interest in hydroxyl groups in cellulose, fiber-starch-fiber bonds are formed, and these bonds may be stronger than fiber-fiber bonds. In addition, very thin fibers remain on the paper surface like fluff due to the effect of static electricity charges, causing fluff. These papers run the risk of scattering the ink and losing dyeing homogeneity. Using starch, fine fibers are also drawn to the surface, making the paper surface smoother. Starch thermal properties and morphological structure vary according to the source from which it is obtained. It was stated that the granular structure of potato starch is larger than that of corn and cassava starch, and it is easier to gel with temperature (Abdullah *et al.,* 2018). In paper production, cooking gelatinization of starch is more effective, and it has been stated that potato starch is more effective than corn starch. Starch mixed in the Hollander tends to separate from the fibers with a mechanical effect. The starch is fixed to the paper by making a strong bond only after drying. This is because starch is not a wet-strength agent. In a study, 1.5 % CS obtained from potato was added to the pulp to produce paper from softwood. It was stated that there was a 64 % increase in the tensile index in the obtained CS-added papers compared to the control samples, and there was no significant difference when increasing the starch ratio (Gülsoy, 2014).

In a study regarding the morphologic properties of Eucalyptus pulp fibers, length (0.70–0.84 mm) and width (18.0–19.1 μm) were specified, and it was stated that papers with good mechanical properties could be obtained (Flávia Morais *et al.,* 2019). Unbleached pulps are difficult to dye because they contain lignin and other impurities. Because of these impurities and lignin, UV–Vis measurements of paper may include systematic errors (Małachowska *et al.,* 2020). On the other hand, bleached and high white pulps are easier to dye than other pulps. The bleached pulp was chosen to accurately determine the effect of dyestuff and mordant.

For a substance to be considered a dyestuff, it must be colored and tightly coupled to the fiber. Red pine bark contains Oligomeric Proantho Cyanidin (OPC). It has been reported that the ratio of OPC is high in the dyestuff that can be separated from the bark of red pine (Demir and Demir, 2012).

In Türkiye, 8,433,852 m^3 debarked Turkish red pine logs were produced in 2019 (OGM, 2020). The red pine bark remaining from this production is left to rot in the forests. Turkish red pine bark is burned after peeling to obtain energy. Although incineration is seen as a solution to energy production and removal of waste bark, emissions released into the atmosphere and some substances that pass into the ash can be problematic in terms of gas and solid waste disposal. For this reason, waste should be converted into useful products instead of incinerated. This will help reduce environmental pollution and positively affect the ecological balance.

Dyes are used traditionally or industrially to manufacture textiles, wood, and paper. In studies made from plant-derived dyestuffs, parts of plants containing chromophores such as bark, leaves, and flowers are used. Due to the low affinity of cellulose towards anionic substances, it must be cationic loaded in case of dyeing with natural dyestuffs. For this purpose, mordant is used. Most natural yellow colors are hydroxy and methoxy derivatives of flavones and isoflavones. Yellow dye mordants were noted to be tin, alum, and chrome (Vankar, 2000). Wastewater treatment from the metal mordants used is very costly. In addition, metal in products dyed for human use adversely affects human health. Instead of metal salts used as mordant in the literature, the dual advantage of using cationic starch, an organic substance, has been considered in this study. This paper aims to improve the paper dry strength properties, while increasing the dyestuff adhesion in the papers to be obtained in this way.

2 MATERIALS AND METHODS
2. MATERIJALI I METODE

2.1 Materials
2.1. Materijali

In this study, the pulp was dyed with natural dyestuff obtained from Turkish red pine (*Pinus brutia* Ten.) bark. In Turkey, the bark cut from coniferous trees is left in the forest after being debarked. For this reason, in our study, no trees were cut for bark production, and the waste bark remaining from log production was used. The Turkish red pine bark was taken from Türkiye's 35.33 longitude and 36.97 latitude region right after the tree was cut. The bark was ground and dried at room temperature, sieved, and the remaining part of the 60 mesh sieve was used. The high lignin concentration in the paper can even suppress some degradation pathways In unbleached pulps, the color of the pulp turns brown depending on the lignin ratio. Therefore, bleached Kraft pulp (21ºSR) obtained from eucalyptus (*Eucalyptus grandis*) wood was used.

2.2 Methods
2.2. Metode

In our study, the 25 g bark sample was mixed with 500 ml of distilled water in a 1000 ml beaker and heated in a thermostated hot water bath with a sensitivity of ±2 ºC for 4 hours at 82 ºC and mixed with a glass baguette every 15 minutes. At the end of the process, the mixture was cooled at room temperature, filtered, and made ready for use as dyestuff. The adhesive properties of CS adequately modified are better than those of natural starch. Modifying starch with different methods can even help adapt it, by considering its properties, for applications in areas such as food and papermaking. (Bismark *et al.,* 2018). Potato was the source of CS used as a mordant in the study. However, writing and printing processes have low ink and chemical costs (Hassaan and Nemr, 2017). The starch ratio was taken as 1.5 % by weight of the oven dry pulp. To prepare the starch solution, 500 ml of distilled water was poured into a 1-liter beaker, 3.6 g of CS was added and mixed in a hot water bath at (95±2) ºC and gelled. To obtain ten handsheets, 50 ml of gelled starch suspension was added and mixed in the mixer. In this case, 0.036 g of completely dry starch is added to 2.4 g of paper. Then, using a laboratory-type Rapid Köthen paper machine, paper groups with (75±2) g/m^2 were obtained according to ISO 5269-2 standard (ISO 5269-2, 2013).

The papers obtained were conditioned according to TAPPI T 402 sp-03 (2003) standard. The tensile properties of the paper are measured according to the TAPPI T 494 om-01 (2001) standard.

The morphological features of the papers and how the starch forms a bridge between the fibers were visualized in SEM. By measuring the ΔL, Δa, Δb, and, ΔE values of the obtained paper groups after UV, the dyestuff ratio and the effect of cationic starch were determined. Test sample color measurements before and after accelerated aging were made with Konica Minolta CD-600 colorimeter in accordance with ISO 7724 standard (ISO 7724-1, 2, 3, 1984). Accelerated weathering (50 ºC, 0.75 W/m^2) test was carried out on Q-Panel Lab Products instrument according to Eser and Önal, 2015. The dyed paper aging (UV) treatment was applied at four time intervals: 24, 48, 96, and 120 hours. The tests were carried out at 50 ºC while UV treatment was applied; no other conditioning process was applied.

3 RESULTS AND DISCUSSION
3. REZULTATI I RASPRAVA

3.1 Morphological analysis
3.1. Morfološka analiza

A low L^* value means a high dye yield. Compared to the reference sample, a higher L^* value indicates a brighter appearance and lighter color, while a lower L^* value indicates a duller and darker color. Paper groups and their $L^*a^*b^*$ values are given in Table 2.

In the samples without starch and dyestuff, yellow was at low values, and red was not observed. The red color was also observed with the addition of dyestuff, and the red and yellow color tone became darker with the increase in the amount of dyestuff. These colors are even darker in the samples with the same amount of dyestuff with starch added. The low L value, proof of dye adhesion, showed a rapid decrease with adding 50 ml of dyestuff. The lower L value of the same amount of dyestuff-added papers with starch added is proof that starch increases dye adhesion. As the amount of dyestuff was increased by more than 50 ml, the decrease in L value was not much. Therefore, the optimum value of the amount of dyestuff can be accepted as 50 ml. This is also seen in the red color change. There is an increase in yellow-colored CS-added papers samples at high dyestuff usage. This is because starch increases adhesion. This is also confirmed by the fact that the yellow color of C2 is more dominant than the green. After the UV treatments, the color measurements of the dyed papers were made by spectroscopy. The results obtained from the color measurements are shown in Table 3.

Table 3 shows that the yellow color (+Δ*b**) turned into blue color (-Δ*b**) after 24 hours of UV application on papers dyed with mordant-free dyestuff. In papers using cationic starch, the color transformation occurred after 96 hours. This shows that starch is effective as a mordant and that its UV resistance is greater

Table 1 Paper groups; suspension was mixed by mixer at low speed
Tablica 1. Skupine papira (suspenzija je malom brzinom izmiješana u mikseru)

Groups / *Skupine*	**Abbreviation** *Kratica*	**Explanation** / *Objašnjenje*
Control 1 / *kontrolna skupina 1.*	C1	Test papers were made without starch and dye *ispitni papiri bez škroba i bojila*
Control 2 / *kontrolna skupina 2.*	C2	Starchy papers were obtained by adding only gelled CS *papiri s dodatkom samo želiranoga kationskog škroba*
Only dyed papers *samo obojeni papiri*	D50	50 ml of dyestuff was added *s dodatkom 50 ml bojila*
	D100	100 ml of dyestuff was added *s dodatkom 100 ml bojila*
Dyed CS-added papers *obojeni papiri s dodatkom kationskog škroba*	D50+CS	50 ml of dyestuff and 1.5 % of CS were added *s dodatkom 50 ml bojila i 1,5 % kationskog škroba*
	D100+CS	100 ml of dyestuff and 1.5 % of CS were added *s dodatkom 100 ml bojila i 1,5 % kationskog škroba*

Table 2 Paper groups and their $L^*a^*b^*$ values
Tablica 2. Skupine papira i njihove $L^*a^*b^*$ vrijednosti

Paper groups *Skupine papira*	**Dyestuff, ml** *Bojilo,* ml	**Cationic starch, %** *Kationski **škrob**, %*	L^*	a^*	b^*
Control 1 (C1) *kontrolna skupina 1. (C1)*	0.0	0.0	91.58	-0.14	2.16
Control 2 (C2) *kontrolna skupina 2. (C2)*	0.0	1.5	89.31	-0.38	3.34
Only dyed papers (D50) *obojeni papiri (D50)*	50	0.0	76.45	8.46	14.49
Starchy dyed (D50+CS) *obojeni papiri uz dodatak škroba (D50+CS)*	50	1.5	70.96	9.56	16.55
Only dyed papers (D100) *obojeni papiri (D100)*	100	0.0	75.73	9.00	15.50
Starchy dyed (D100+CS) *obojeni papiri uz dodatak škroba (D100+CS)*	100	1.5	70.20	9.77	20.18

Table 3 $\Delta L^*\Delta a^*\Delta b^*$ values after UV treatment
Tablica 3. Vrijednosti $\Delta L^*\Delta a^*\Delta b^*$ nakon UV tretmana

Paper groups *Skupine papira*	**UV, hours** *UV, sati*	**ΔI***	**Δ*a***	**Δ*b***	**Δ*E****
Control 1 (C1) *kontrolna skupina 1.*	24	-0.33	-0.14	0.61	0.99
	48	0.38	-0.18	-0. 10	0.77
	96	0.90	-0.17	-0.23	0.87
	120	1.40	-0.15	-0.40	1.20
Control 2 (C2) *kotrolna skupina 2. (C2)*	24	0.98	-0.75	1.51	0.90
	48	1.20	-0.83	1.00	0.86
	96	2.34	-0.88	-1.60	1.34
	120	2.61	-0.90	-2.78	1.54
Only dyed papers (D50) *obojeni papiri (D50)*	24	2.69	-2.44	-0.11	1.24
	48	5.29	-3.73	-1.62	2.21
	96	8.49	-5.46	-3.15	4.02
	120	9.45	-5.60	-3.87	4.74
Starchy dyed (D50+CS) *obojeni papiri uz dodatak škroba (D50+CS)*	24	3.00	-2.70	2.04	4.17
	48	5.53	-3.10	0.30	6.48
	96	8.60	-5.27	-3.16	10.58
	120	9.55	-5.63	-3.89	11.50
Only dyed papers (D100) *obojeni papiri (D100)*	24	4.24	-3.18	-1.02	2.55
	48	5.63	-3.43	-1.51	3.10
	96	7.68	-5.50	-2.33	9.25
	120	9.61	-6.10	-3.00	11.40
Starchy dyed (D100+CS) *obojeni papiri uz dodatak škroba (D100+CS)*	24	4.24	-3.25	2.51	4.66
	48	5.63	-3.43	1.02	5.85
	96	7.68	-5.50	-2.33	10.42
	120	9.61	-6.10	-3.00	11.61

for 72 hours. When Δa values were examined, it was observed that the results were negative (-). It has been determined that the values of paper groups using starch are higher, especially when adding the same amount of dyestuff. The increase in Δa values to minus (-) indicates that the colors of post-UV dyed papers move towards darker shades of green. In a study conducted on onion skin dyestuff, after 12 days of aging, the a^* value increased and shifted from green to red (Akyol and Çakar Sevim, 2023).

A decrease in the ΔE value means that the compared colors are getting closer, and an increase in its value means that the colors are moving away from each other. It was determined that the lowest/highest ΔE^* values of 50 ml dyed and starch-free papers were 1.24/4.74, respectively. It was observed that ΔE values increased as UV duration increased. Therefore, as the aging time increased, the colors diverged from each other. It was determined that D50+CS paper groups had a score of 4.17, and D100+CS had a score of 4.66.

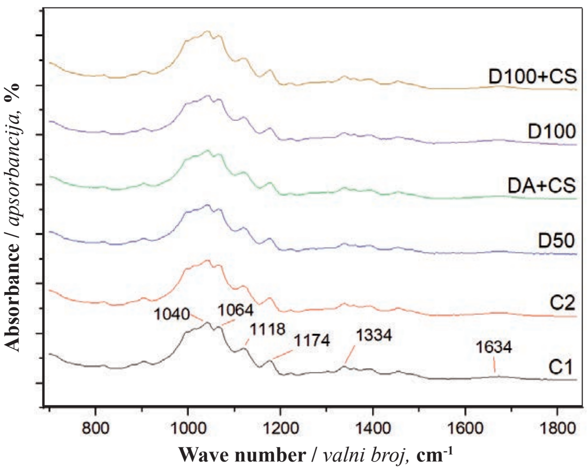

Figure 1 FTIR results of samples
Slika 1. Rezultati FTIR-a

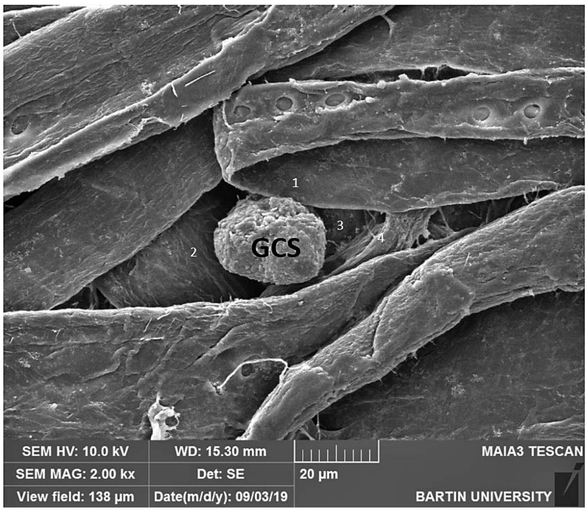

Figure 2 SEM images of samples (GCS – Gelled cationic starch, 1, 2, 3, 4 – Gelled cationic starch bridges with fibers)
Slika 2. SEM slike uzoraka (GCS – želirani kationski škrob, 1, 2, 3, 4 – želirani kationski škrobni mostovi s vlaknima)

Figure 1 shows the FTIR results of the obtained papers.

Figure 1 shows that there is no difference between the papers along the *x*-axis. It can be seen that there are differences in the y-axis due to the difference in color tones. In the figure, the formation of a higher peak in the same wavelength range as the amount of dyestuff increases is due to intensity. This is because there are darker shades of the same color.

It is seen that the addition of dyestuff does not affect the tensile effect of the paper. The reason for this can be explained by the fact that dyestuffs do not have a positive effect because they are not dry-strength substances, they are not the size of a filler, and they do not harm the connection between fibers.

Figure 2 shows the surface SEM image of the gelled cationic starch (GCN) added paper obtained at 27 ºSR from bleached pulp obtained from eucalyptus wood by the Kraft method.

The polar hydroxyl groups present in starch increase the strength of the paper by forming 'fiber-starch-fiber' bonds with the hydroxyl groups in cellulose fibers (Casey, 1960). Figure 2 shows that starch settles in the space of the paper and forms an interfiber bridge there. In our study, there was a 38 % increase in tensile index with the addition of 1.5 % cationic starch, thanks to the bonds made by cationic starch in contact with at least four (1-2-3-4) fibers at the same time on the visible surface. Additionally, it is noteworthy that it fills the space between fibers. This will also have a positive effect on increasing surface smoothness. In addition, the roughness of the starch surface due to gelation increases the contact area. In the literature, it is stated that the average tensile index of papers produced at 27 ^{0}SR from bleached eucalyptus pulp without a dry strength agent is 41.3 Nm/g (Gonzàlez *et al.,* 2012). This study determined the tensile index as 44 (N·m/g) in starchless paper groups at 21 ^{0}SR. The difference occurs with the increase in the amount of beating.

4 CONCLUSIONS
4. ZAKLJUČAK

When starting this study, the aim was to provide an alternative dyeing to synthetic dyes and inorganic mordants in paper dyeing. For this purpose, Turkish red pine bark extract was chosen as the natural dyestuff in paper dyeing. Cationic starch was used as a mordant. It aimed to increase the dry strength properties of the paper with the same mordant while increasing the dye adhesion by taking advantage of its adhesive properties.

The degree of paint adhesion is the ΔL^* value. The fact that this value is higher than the control samples means that adhesion increases. ΔL^* values in paper groups obtained using Turkish red pine bark extract and cationic starch together are significantly higher than in paper groups without cationic starch. This is because starch works well as an organic mordant. There was no significant increase in ΔL^* values by increasing the amount of dyestuff from 50 ml to 100ml in mordant samples. Therefore, the optimum amount of dyestuff can be considered to be 50 ml. When Δb values are examined, it has been observed that it gives different results than Δa^* values. At ΔE^* values, it was determined that the average of starch paper groups was 248.70 % higher than the average of non-starch paper groups. It has been observed that cationic starch, together with the natural dyestuff of Turkish red pine bark, adheres well to the paper pulp. The use of cationic starch has made a significant difference in the adhesion of the natural dyestuff of Turkish red pine bark to papers produced from wood pulp before UV and after UV and in increasing the durability of the paper. These findings will contribute to the literature and be useful to future studies.

In this study, it was seen that natural wastes such as Turkish red pine bark can be converted into benefits and, if used, become an important biomass. We believe that Turkish red pine bark can be used in the board industry or agricultural applications since it does not lose significant mass after obtaining natural dyestuff.

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Corresponding address:

CENGIZ KEŞMER
Çukurova University, Aladağ Vocational High School Forestry Department, Adana, TURKEY, e-mail: