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Oleksandra Voronych[1], Sergiy Kurta[1], Volodymyr Starchevskyy[2] and Sofiya Fedorchenko[1]

TECHNOLOGY OF RECYCLING, PROPERTIES AND USE OF POLYVINYLCHLORIDE-COATED PAPER WASTE

[1]Vasyl Stefanyk Precarpathian National University
57 Shevchenko St., Ivano-Frankivsk, 76018, Ukraine; sasha.voronych@gmail.com;kca2014@ukr.net
[2] Lviv Polytechnic National University, 12 S. Bandera St., 79013 Lviv, Ukraine

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Abstract. The technology of recycling of polymer-coated paper waste is described. Physical and chemical properties of fibers obtained from wallpaper wastes and from their derivative compositions were investigated. A special crusher with primary and secondary grinding stages and with a section for separating paper fibers from polymer coating was designed. Industrial trials of cellulose obtained from wallpaper wastes for the asbestos cement sheets manufacturing were held. Its impact on the quality and physical and mechanical properties of sheets was shown. Methods of thermogravimetry, microscopy, and differential thermal, infrared spectral and chemical analysis were applied to investigate cellulose fibers derived from recycled wallpaper. Their properties were compared to the natural cellulose and polyvinylacetate fibers, which are used in the production of asbestos cement sheets.

Keywords: wastepaper, grinding, separation, recycling, cellulose fiber, polymer coating.

1. Introduction

In the production of polymer-coated decorative wallpapers in Ukraine (EDEM PJSC, Sintra Ltd., TM “Vernissage”, LLC “Krokus”, TM “Slavik Wallpapers”), up to 5–10 % of products are wasted [1] – defective by colour or quality products. According to the technology of production, these rolls are made of paper (pulp or non-woven base) covered with polyvinylchloride (PVC) polymer. Polymer coating consists of dyes, inorganic fillers and foaming agents [2]. High mass content of PVC makes it difficult to proceed with mechanical sorting and disposal of such wastes by burning because it causes the release of a large amount of harmful chlorine compounds such as hydrogen chloride and even dioxins into the atmosphere [3]. Therefore, the development of technology for the processing of waste products to separate polymer coating from paper substrate is crucial. The existing methods allow separating polymer coating from cellulose fibers in a liquid phase [4]. This is a time-consuming and costly way, which generates another kind of liquid wastes that require disposal [5]. Furthermore, cellulose obtained in such a way is of an extremely poor quality.

In this article, we propose a method that involves mechanical grinding and dry separation of loosened particles of crushed cellulose and polymeric PVC coating fractions [6]. Grinding is carried out in two stages. At Stage 1, cutting mills are used, and Stage 2 includes the use of a flat-knife hammer crusher.

2. Experimental

The newly developed technology implies the use of two types of crushers for the recycling of defective wallpaper rolls (wastes of “Sintra,” Limited Liability Company (LLC), in Kalush, Ukraine) [5]. At Stage 1, they were cut with the help of chopping-cutting type of crushers. At Stage 2, the paper wastes were processed in the drum crushers where the separation of cellulose fibers from polymer coating occurred.

The experiment was conducted both in the laboratory and with the specially designed industrial crushers, which afforded combining of all stages: crushing, separation, and purification of fibers in the air flow (Fig. 1) [6].

In order to recycle cellulose and paper waste with polymer coating, wallpaper rolls were first (Fig. 1, pos.11) supplied with the belt-fed conveyor (Fig. 1, pos.10), which was situated on the same level with the primary chopping-cutting crusher (Fig. 1, pos.9), perpendicular to the knives that were attached to the rotor. Further, to purify crushed wallpaper particles from metal impurities, they were delivered to the magnetic separator *via* connecting channel (Fig. 1, pos.12) and to the secondary crushing knife or flat-hammer drum (Fig. 1, pos.2) with the centrifugal fan at the output (Fig 1, pos.3).

The centrifugal fan was connected to the crushing drum (Fig. 1, pos.2) through the central axial hole that was covered with drum knives or hammers in the axial direction. With the help of the complex crusher (Fig. 1), the waste paper was cut and torn with the secondary knife or hammer type crusher at 1500–3000 rpm with slight decrease in fiber length, which afforded high quality cellulose fibers, which could further be used for paper manufacturing. To simplify the process of separating loosened cellulose from polymer coating, the complex crusher was equipped with cyclone and textile-sleeve filter (Fig. 1, pos.4, 7) .

Under the laboratory conditions, the separation of cellulose fibers from polymer coating was performed on sieves with holes of 4 different diameters (mm): 5; 2; 1; <1.

Obtained cellulose fibers (cellulose from coniferous species of wood – 79 %; pulp of hardwood – 5 % and polyester fiber – 16 %) were used in the production of asbestos cement sheets, which are commonly used for covering roofs. Asbestos cement is a building material made from an aqueous mixture of cement and asbestos.

During the formation of asbestos cement sheets with loosened cellulose obtained from wallpaper rolls waste instead of natural cellulose, the following parameters were received: rolling sheet humidity 25 %; raw sheet density 1.52 g/cm^3, and residue concentration at the outgoing from bath water – 3.0; 3.9 and 4.9. During the formation of sheets with the addition of natural cellulose, the parameters were as follows: rolling sheet humidity 22–24 %, raw sheet density 1.52–1.54 g/cm^3, and residue concentration in the water from the baths – 3.0. As we can see, all the parameters fit to the regulations of JSC "Ivano-Frankivskcement" [7]. The tests showed that even unseparated crushed waste products can be used as a part of asbestos cement sheets with the weight proportion of about 5–10 %. Moreover, the physico-mechanical and technological properties of asbestos cement sheets were not affected. On the contrary, the content of other additives in the sheets decreased. Finally, by substantially reducing the prices of these cellulosic waste products, when compared with the price of indicated natural supplements, the significant economic impact can be achieved. Through the reduction of asbestos content, it is possible to decrease the toxicity and other harmful effects of asbestos cement sheets on the environment.

Through the application of infrared spectroscopy and thermal analysis, the experiment was conducted to investigate natural cellulose fibers used at JSC "Ivano-Frankivskcement" for filling the asbestos cement sheets and the fibers obtained from the wastes that had been modified with water-repellent agents.

For the thermal analysis, the pressed samples were crushed into pieces, and the fraction with particles size of 0.5–1 mm was selected. Thermal studies were performed with Q-1500 IOM derivatograph (Hungary) with the computer data registration at 288–1273 K. Heating rate was 10 deg/min. Simultaneously, the curves of the differential thermal analysis (DTA), thermogravimetric curve (TG) and differential thermogravimetric curve (DTG) were recorded.

Infrared (IR) transmittance spectra at 4000–400 cm^{-1} were recorded using Thermo Nicolet Nexus FT-IR spectrometer (silica: KBr = 1: 10).

3. Results and Discussion

Results of industrial processing of defective wallpaper rolls with and without PVC coating are shown in Table 1.

As shown in Table 1, crushing and separation of different products in the above described crusher run more efficiently. It ensures a higher yield of loosened cellulose and polymer particles with minimal losses that do not exceed 5 %, in contrast to other existing methods [9] where losses reach 20–40 %. The samples of products are shown in Fig. 2.

Loosened cellulose received from crushed wallpaper rolls waste of LLC "Sintra" (Kalush, Ukraine) was tested on the industrial equipment for receiving asbestos cement sheets at JSC "Ivano-Frankivskcement". The results of physical and mechanical tests of asbestos cement sheets received with loosened cellulose fibers and obtained from crushed waste wallpaper rolls are shown in Table 2 .

Table 2 shows that the sheets produced through this method met the parameters of the technical specifications for asbestos cement sheets and can be used in construction.

Partial decrease of physical and mechanical parameters of asbestos cement sheets as presented in Table 2 occurs due to the partial length reduction of cellulose fibers during mechanical processing of wallpaper wastes as well as due to the random positioning of fibers with remaining 5–10 % PVC particles and irregular shape of the cellulose fibers in comparison to polyester fibers which are also used in the production of asbestos cement sheets (Fig. 3).

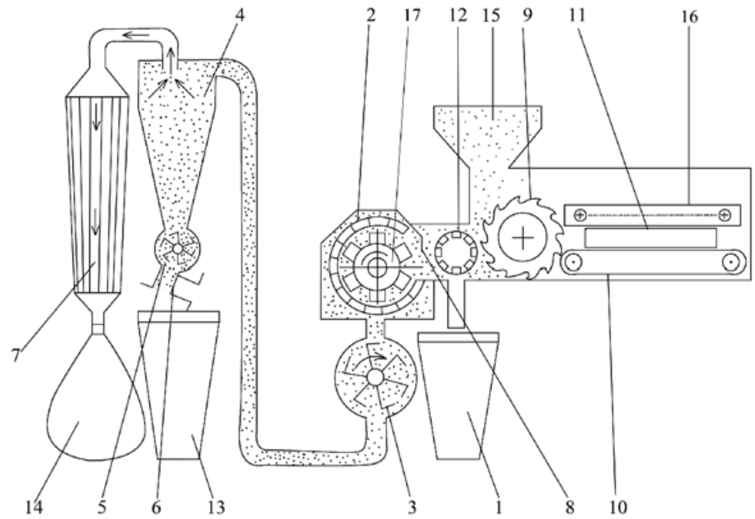

Fig. 1. Technical chart of a complex crusher of paper waste: bunker for metal contaminants (1); crushing knife or flat-hammer drum (2); centrifugal fan (3); cyclone (4); bellmouth (5); floodgate (6); filtering textile sleeve (7); damper (8); chopping-cutting knives (9); belt-fed conveyor (10); wallpaper rolls (11); magnetic separator (12); bunker for polymer particles (13); textile bag for cellulose (14); small hopper for receiving waste paper products (15); adjustable pushing device (16) and rotor (17)

Table 1

Results of industrial processing of defective wallpaper rolls with and without PVC coating

Type of waste	Speed of the primary crusher, rpm	Speed of the secondary crusher, rpm	Size of particles of paper waste after the primary crusher (width: height), mm	Size of particles of paper waste after the secondary crusher (width: height), mm	Size of polymer particles after the secondary crusher (width: height), mm	Mass content of polymer particles, %	Mass content of cellulose fibers, %	Mass content of pure cellulose in separated wastes, %
Wallpaper Type 1 (PVC content – 50 %)	1000	3000	(10–40): (300–1000)	(0.1–1): 0.01–0.1)	0.5–10	45–49	45–49	90–97
Wallpaper Type 1 (PVC content – 25 %)	1000	2000	(10–40): (300–1000)	(0.1–1): (0.01–0.1)	0.5–5	20–23	20–24	85–95
Wallpaper Type 1 (PVC content –5 %)	750	1500	(10–40): (100–500)	(0.05–0.5): (0.01–0.1)	0.1–1.0	2–4	94–98	85–90
Waste paper (PVC content – less than 5 %)	500	1000	(10–40): (100–500)	(0.05–0.25): (0.01–0.1)	0.1–1.0	1–4	95–99	80–85

a) b) c)

Fig. 2. Pictures of crushed wallpaper wastes: unseparated crushed wastes (a); purified cellulose(b) and PVC particles (c). Image scale 1: 1

Table 2

Physical and mechanical properties of asbestos cement sheets produced with cellulose fibers received from wallpaper wastes

No	Parameter	Units	Parameters according to the regulations of JSC “Ivano-Frankivskcement”	Samples (1) obtained through the addition of fibers received from wallpaper wastes	Samples (2) obtained through the addition of natural cellulose
1	Planck’s loading (after 7 days)	N/m	not less than 2500	3826	4262
2	Planck’s loading (after 14 days)			3309	4262
3	Planck’s loading (after 28 days)			3558	4262
4	Ultimate bending strength (after 7 days)	MPa	not less than 160	206.9	175.5
5	Ultimate bending strength (after14 days)			169.7	175.5
6	Ultimate bending strength (after28 days)			166.4	175.5
7	Bending strength (after 7 days)	N/m	not less than 40	79.3	76.2
8	Bending strength (after 14 days)			68.7	76.2
9	Bending strength (after 28 days)			63.3	76.2
10	Density (after 14 days)	g/cm^3	not less than 1.6	1.64	1.669
11	Density (28 after days)			1.67	1.669
12	Impact strength (after 7 days)	kJ/m^2	not less than 1.4	1.9	2.19
13	Impact strength (after 28 days)			1.88	2.19

a) b) c)

Fig. 3. Microphotographs cellulose fiber obtained during the grinding wastes wall (a), natural fiber paper (b) and PVA fiber used in "Ivano-Frankivsk" (c) to get asbestos cement roofing slate. The sizes of cellulose fibers were: L = 0.1–1 mm; D = 0.01–0.1 mm. Photos were taken with RV-3320 microscope (image scale 1:100)

The results received from IR transmittance spectrum (Fig. 4) and TG (Fig. 6) tests support our hypothesis of an additional length reduction and stratification of cellulose fibers during the dry mechanical grinding of wallpaper wastes.

The wide line of absorption at 3350 cm^{-1} of cellulose IR transmittance spectrum (Fig. 4) is related to the valence vibrations of hydroxyl groups included in hydrogen bonds. At 2900–2800 cm^{-1}, the valence vibrations of C–H bonds of cellulose methyl and methylene groups were observed. At the spectrum of modified cellulose, such valence vibrations overlap with the absorption of CH_3-groups, which are a part of dimethyl silica coating of cellulose fibers. This leads to the increase in intensity of the absorption lines at 2900 cm^{-1} due to the fact that the additional CH_3-groups get attached to the surface of cellulose during its interaction with the modifier agent – dimethyldichlorosilane. Vibrations of C–H bonds are also apparent at the spectrum at 1470–1430 cm^{-1} and 1380–1370 cm^{-1}. Reducing the intensity of the absorption line of the modified compared to unmodified cellulose is associated with the decrease in the degree of cellulose crystallinity as a result of chemical modification.

The line at 1150 cm^{-1} in the IR transmittance spectrum of cellulose is associated with the valence vibrations of C–O–C ether bonds of cellulose fibers cyclic structure. It is much stronger for natural uncrushed cellulose than for crushed cellulose fibers (Fig. 4). That is probably due to the rupture of bonds during crushing of cellulose as shown in the reaction (Fig. 5) [10-14]. At the same time, this line substantially shifts to 1125–1025 cm^{-1} and increases in intensity up to 20–30 % during the interaction of dimethyldichlorosilane modifier with cellulose –C–OH surface groups which are formed at broken bonds of cellulosic residues of six-member cycles.

The line at 1100 cm^{-1} corresponds to asymmetric synphase valence vibrations of the cycle. Meanwhile, the absorption lines at 1020–1100 cm^{-1} are typical for valence vibrations of siloxane bonds. This explains the increase in the intensity of absorption lines in this area for cellulose, modified according to Eq. (1).

$$\text{Surface/cellulose –C–OH} + (CH_3)_2SiCl_2 \leftrightarrow$$
$$\leftrightarrow \text{surface/cellulose –C–O–}SiCl(CH_3)_2 + HCl \quad (1)$$

The lines at 1750 cm^{-1} of crushed cellulose spectrum correspond to carbonyl groups which can be formed after breaking ether bonds of six-membered cellulose cycles (Fig. 4). This line appears in the spectra of cellulose obtained during the crushing wallpaper wastes that may indicate the destruction of chemical bonds of cellulose residues of six-membered cycles during mechanical processing of cellulose.

These data were also confirmed by thermogravimetric analysis (Fig. 6). The cellulose sample obtained from wallpaper wastes starts to lose water during dehydration and decarboxylation at the temperature which is 5–10 degrees lower when compared to naturall cellulose sample (Table 3), and the maximum decomposition temperature for cellulose obtained from wallpaper wastes is 563 K, which is much lower than 598 K for natural cellulose.

Mass losses during the decarboxylation of cellulose waste are lower than those from natural cellulose, where the overall mass loss reaches 99 %, while they make up only 91 % for cellulose from wastes (Table 3).

All this evidence supports our assumption regarding partial degradation of cellulose chemical bonds in the process of mechanical grinding of wallpaper wastes.

Dehydration, decarboxylation, and degradation temperatures of modified cellulose decrease even more in comparison to the unmodified natural and even mechanically crushed cellulose, which is associated with low strength of a bond between the modifier and cellulose fiber surface after the chemical treatment.

The high value of final temperature of decomposition of cellulose waste is 963 K (Fig. 6) while it is 753 K for natural cellulose due to the presence of PVC and inorganic impurities such as calcium carbonate and titanium dioxide. These inorganic fillers do not completely decompose by heating, which results in a higher content of total residue after calcination for the cellulose derived from wallpaper wastes.

The modified samples after the prior chemical treatment also have lower temperatures of decarboxylation and destruction than the waste cellulose and natural cellulose samples, indicating the partial destruction of the structure in the modification process (Table 3). Hydrophobization efficiency is confirmed by the data shown in Table 4, which compares water absorption [15] and moisture absorption [16] for modified and unmodified fibers.

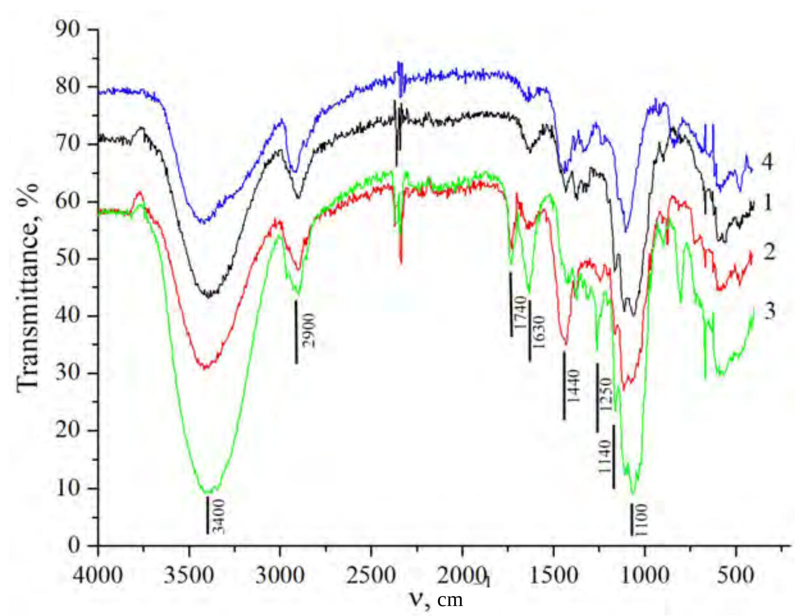

Fig. 4. IR transmittance spectra of cellulose fibers used for the asbestos cement sheets manufacturing: natural cellulose fibers used to manufacture asbestos sheets (1); cellulose fibers derived waste recycling wallpaper (2); cellulose fibers derived waste processing wall whose surface modified silicon water repellents (3) and polyvinyl acetate fibers used to manufacture asbestos sheets (4)

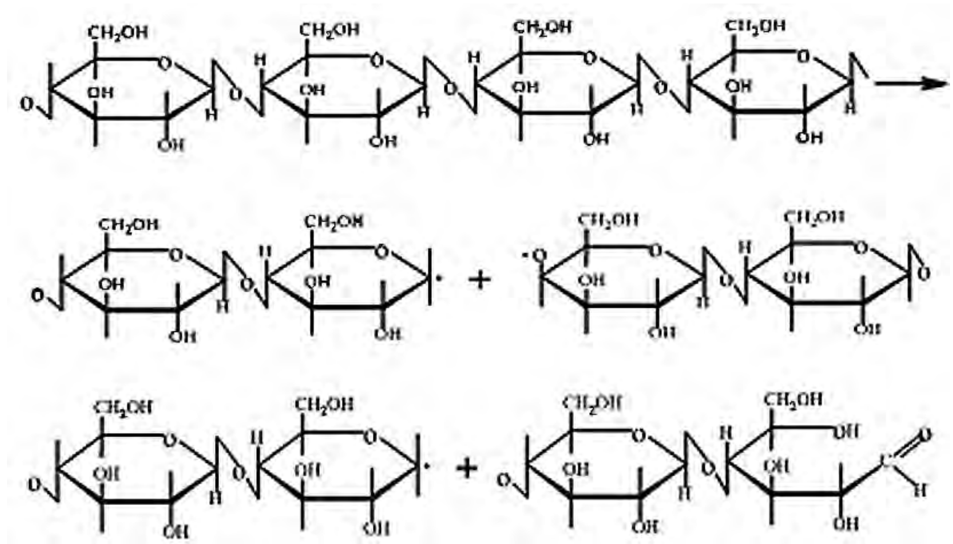

Fig. 5. Breaking of ether bonds of six-member cellulose cycles during mechanical grinding

Table 3

Results of thermogravimetric examination of cellulose and polyvinyl acetate samples

Parameter	Natural cellulose from JSC "Ivano-Frankivskcement"	Cellulose from crushed wallpaper waste	Modified silicon cellulose from wallpaper wastes	PVA fiber from JSC "Ivano-Frankivskcement"
Temperature indicators				
Maximum temperature of dehydration, K	353	348	358	363
Temperature of cellulose decarboxylation and degradation, K	523	513	463	518
Temperature of the maximum rate of decarboxylation and degradation of cellulose, K	598	563	548	633
Temperature of carbon formation, K	723	733	683	703
Final temperature of carbon formation from cellulose, K	753	963	843	873
Indicators of mass losses				
Mass losses during dehydration of cellulose, %	8	8	8	4
Mass losses from decarboxylation and degradation of cellulose, %	65	45	37	44
Mass losses from the complete degradation of cellulose, %	99.0	91.5	93.3	100
Time and speed indicators				
Cellulose dehydration rate, mg/min	0.82	0.81	0.675	0.50
Decarboxylation rate, mg/min	2.64	2.34	1.22	1.06
Degradation rate, mg/min	1.08	0.53	0.98	1.34
Average rate of decomposition of cellulose, mg/min	1.16	0.77	0.99	0.90
Cellulose dehydration start time, min	5	4	4	4
Cellulose decarboxylation start time, min	16	14	10	16
Cellulose degradation completion time, min	42	66	51	56

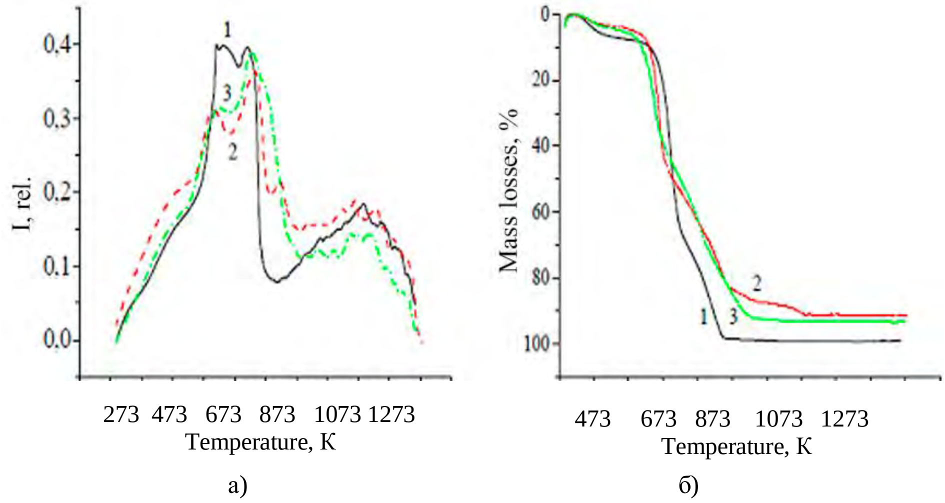

Fig. 6. DTA (a) and TG (b) fibers diagrams: natural fibers (1); fibers obtained from wallpaper wastes (2) and modified silicon fibers (3)

Table 4

Properties of modified and unmodified fibers

Parameter	Unmodified fiber	Modified silicon fibers
The residue after calcinations at 1073 K, %	4.051	16.252
Moisture absorption, %	6.2	3.2
Water absorption, %	520	80

4. Conclusions

1. Grinding and separation of fractions is more effective with the use of the described crusher. It ensures a higher yield of loosened cellulose and the particles of polymer coating with minimal losses that do not exceed 5 %.

2. The proposed technology of crushing and separation of two different fractions (polymer coating and loosened cellulose fibers) affords the higher purity of both fractions reaching 85–97 % for the wallpaper with PVC coating for loosened cellulose.

3. The structure of cellulose fibers changes during crushing of wallpaper rolls. They get partially reduced and deformed with the rupture of chemical bonds of cellulose fibers leading to changes in cellulose properties. This is confirmed by the results from thermal and spectral analysis and by changes in physical and mechanical properties of asbestos cement sheets.

4. Based on the results of this study, the loosened cellulose can be used as the reinforcing filler for asbestos cement sheets and other products due to its improved hydrophobization, lower humidity and water absorption of fibers.

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ТЕХНОЛОГІЯ РЕЦИКЛІНГУ, ВЛАСТИВОСТІ ТА ВИКОРИСТАННЯ ПАПЕРОВИХ ВІДХОДІВ З ПОЛІВІНІЛХЛОРИДНИМ ПОКРИТТЯМ

Анотація. *Описано технологію рециклінгу целюлозних волокон паперової основи та його полімерного покриття, одержаних при переробці-подрібненні целюлозо вмісних шпалер з полівінілхлоридним покриттям внаслідок його відділення від паперової основи. Описані фізико-хімічні властивості волокон та композицій на їх основі при повторному їх використання – рециклінгу. Сконструйовано спеціальну 5-ти стадійну 2-модульну дробарку з первинним і вторинним подрібненням та відділенням-сепарацією паперової основи від полімерного покриття і очисткою повітряного потоку. Проведено промислове випробування одержаної таким чином з відходів шпалер розпушеної целюлози для виготовлення листів азбестоцементного шиферу і показано їх вплив на якість та фізико-механічні характеристики шиферу. Методами термогравіметрії, диференціального термічного, ІЧ-спектрального, хімічного аналізів та мікросконії вивчено волокна целюлози, одержані від переробки відходів шпалер, та порівняно їх властивості з природними целюлозними та ПВА волокнами, що використовуються у виробництві азбестоцементного шиферу.*

Ключові слова*: шпалери, подрібнення, сепарація, рециклінг, целюлозні волокна, полімерне покриття.*