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IR-SPECTROSCOPIC ANALYSIS OF INTERACTION WITH MULTI-LAYER PAPER AND CARDBOARD CONTAINING SYNTHETIC FIBERS WITH PRINTING INKS

Annotation. An IR spectroscopic analysis of the printing and technical properties of new types of multilayer packaging paper and cardboard containing waste polyacrylonitrile fiber and their interaction with printing inks was carried out. The preference for using multilayer composite paper and cardboard for the printing and paper industries is shown. It has been established that the tensile strength of paper does not depend on the strength of individual components, but on the strength of the paper structure formed during its production. When the paper contained 20% waste modified polyacrylonitrile, maximum optical density was achieved with a minimum thickness of the ink layer, that is, saturated prints were obtained with minimal consumption of printing ink.

Keywords: cotton pulp, paper, cardboard, printing, printing ink, printing material, copy, optical density

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ИК-СПЕКТРОСКОПИЧЕСКИЙ АНАЛИЗ ВЗАИМОДЕЙСТВИЯ МНОГОСЛОЙНОЙ БУМАГИ И КАРТОНА, СОДЕРЖАЩИХ СИНТЕТИЧЕСКИЕ ВОЛОКНА, С ПЕЧАТНЫМИ КРАСКАМИ

Аннотация. Выполнен ИК-спектроскопический анализ печатно-технических свойств новых видов многослойной упаковочной бумаги и картона, содержащих отходы полиакрилонитрильного волокна, и их взаимодействия с типографскими красками. Показана целесообразность использования многослойной композитной бумаги и картона для полиграфической и бумажной промышленности. Установлено, что прочность бумаги на разрыв зависит не от прочности отдельных компонентов, а от прочности структуры бумаги, образующейся в процессе ее производства. При содержании в бумаге 20 % отходов модифицированного полиакрилонитрила достигалась максимальная оптическая плотность при минимальной толщине красочного слоя, то есть получались насыщенные оттиски при минимальном расходе типографской краски.

Ключевые слова: бумажная масса, бумага, картон, печать, типографская краска, полиграфический материал, печатный оттиск, оптическая плотность

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Introduction. Today in global world the range of competitive products in the production of pulp-paper and printing products in the world is expanding, producing high-quality ecological products using local and natural raw materials, using new types of raw materials and innovative technological solutions, conducting research and development activities aimed at improving the quality of new types of wrapping paper and reducing the consumption of raw materials.

In this regard, in the Republic of Uzbekistan, due to the increasing requirements for packaging products in the printing industry, special attention is paid to extensive scientific work on the development of new types of such materials and the continuous improvement of their properties [1].

Comprehensive measures are being taken in our republic to fill the domestic market with import-substitute printing products and increase their competitiveness, at the expense of production of new types of products, reduction of product costs, production of new types of paper and cardboard intended for packaging, using local raw materials, and certain results are being achieved [2–3].

The main goal of this work are: to save valuable cotton cellulose, to improve the technology of obtaining multi-layer composite paper and cardboard for packaging products using local textile waste, to study the laws of interaction of different fibers with each other and with polymers, as well as with dyes during the printing process.

Materials and methods. In the following experimental work, multi-layer composite paper and cardboard were prepared using primary and secondary fiber materials and polymers. Preparation of paper samples and evaluation of their physical and mechanical properties was carried out in the testing laboratory of JV Global Komsco Daewoo according to the approved technological regulation.The degree of crushing of the pulp, which describes the ability of the pulp to give moisture in the webs of the paper casting equipment, is one of its most important characteristics, and it was determined on the "Massrolle-22.5" device.

Preparation of multi-layered paper and cardboard samples for packaging products with a mass of 150 g/m^2 was carried out on the «Rapid» (Germany) machine. Cotton cellulose, kaolin, unifloc, rosin glue, aluminum sulfate, and an aqueous solution of recycled secondary polyethylene terephthalate were used to obtain multi-layer composite paper and cardboard [4–7].

In the preparation of paper and cardboard samples, cellulose was ground to a crushing level of 40–55 °ShR for the top layer of the composite material and 21–28 °ShR for the bottom layer. Paper castings with a total mass of 150 g/m^2 were prepared from shredded cellulose (upper layer weight 60 g/m^2, lower layer weight 90 g/m^2, Table 1) [8].

Table 1. **Options for the composition of two-layer castings**

Versions №	Composition content		
	Top layer 40–55 °ShR		Bottom layer 21–28 °ShR
	CC*, %	MPAN**, %	MS–5B, %
Sample № 1	100	–	100
Sample № 2	80	20	100
Sample № 3	50	50	100
Sample № 4	30	70	100

*Cotton Cellulose, **modified polyacrylonitrile

In the first option, the upper layer is 100% cotton cellulose and the lower layer is 100 % secondary (waste) waste, in the remaining options, the percentage composition of the main components of the paper composition is varied: cotton cellulose + modified polyacrylonitrile fiber waste + waste paper.

Paper pulp was prepared separately for each layer of multi-layer composite papers. For the production of such papers, two technological systems and two mesh paper casting machines were used. First, the bottom layer is formed. The mass of the upper layer prepared according to the appropriate composition is transferred from the second tank and combined with the lower layer during the formation, and the layers are combined in the pressed state.

The rapid development of printing technologies has led to an increase in the requirements for the printing properties of paper. High requirements for the quality of printing products require paper manufacturers to solve a number of problems related to the printing properties of the produced papers [9]. The rapid development of printing technologies has led to an increase in the requirements for the printing properties of paper. High requirements for the quality of printing products require paper manufacturers to solve a number of problems related to the printing properties of the produced papers.

In the application of newly introduced printing materials to the field of printing, a large part of the work in the field of research of the printing process is devoted to the study of the mechanism of separation of the paint layer between the surfaces that interact during the printing process. In the study of the ink interaction with paper in printing contact, the factors affecting the transfer of ink are studied. They depend on the properties of paper, ink and printing conditions [10].

In the research work, the methods of analyzing the interaction of the printing system components (paper and paint) were used, which allow to evaluate the influence of the factors characterizing the interaction between the printing ink and the surface of the paper. To control the quality of the images printed on the surface of the printed material, an analysis method based on the assessment of optical density was studied (Table 2) [11]. This method allows to measure the color layer in the printed copy in percentages, measure the average level of gray, color uniformity and intensity. In this case, printing properties were determined according to the standard methodology according to "Method of determining printing properties".

Table 2. **Values of optical densities of copies printed on multi-layer paper**

Paper samples																
	№ 1				№ 2				№ 3				№ 4			
The thickness of the paint layer on the copy, μm	1.3	2.1	2.2	2.5	1.3	2.3	2.8	2.6	1.4	2.0	2.4	2.6	1.3	2.2	2.4	2.5
Optical density, $D_{op.}$	1.4	2.0	2.6	2.8	1.6	2.5	2.7	3.0	1.5	1.6	2.4	2.7	1.2	1.4	1.9	2.5
Dye transferr coefficient, R, %	25	48	53	49	40	51	53	52	30	50	53	52	24	49	50	53

Results and discussion. Results and discussion. As can be seen from Table 2, depending on the thickness of the paint layer, a change in the value of the optical density of all samples was observed, in which the smallest value of the paint layer – 1.3 μm corresponds to the value of the optical density of 1.2 for the paper sample № 3. The same optical density is achieved when the thickness of the layer is 1.4 μm. The structure of the paper and its ability to shrink indicate "selective" shrinkage, which is one of the main printing properties that affect the accuracy of images.

In paper sample № 1, the optical density is 1.4 when the thickness of the paint layer is 1.3 μm, and in paper sample № 2, the optical density is 1.6 when the thickness of the paint layer is 1.6 μm. Thus, the distribution of printing ink on the surface of the printed material has a different de-scription, which is characterized by its microgeometry, for example, in the structure of paper sam-ple № 2 with 20 % of modified polyacrylonitrile fiber waste, the maximum optical density is achieved when the thickness of the ink layer is minimal, that is, the consumption of printing ink is minimal as well as sufficient to obtain saturated copies [12].

A decrease in these values was observed in all experimental papers when the dye layer transferred to the samples was 53 %: № 2, № 1, № 3 and № 4. This situation is explained by the fact that during the formation of the layers, as a result of the introduction of 20 % modified polyacrylonitrile fiber waste into the cotton cellulose fibers, the spaces between different fibers are filled, which does not allow the dye pigments to penetrate into the paper pores during the printing process. It was found that paper № 4 (70 : 30 %) has a lower optical density, while paper samples № 2 and № 3 (20 :80 and 50 : 50 %, respectively) do not absorb dyes to the same extent, and an even layer of dye is formed on the surface of the paper. , which ensures that saturated copies are obtained. This condition indicates that these paper samples have a sufficiently smooth surface. The pigment of the printing ink does not penetrate into the pores of the paper structure after binding and remains on the surface and ensures high optical density of the copy. An IGT model test copy press was used to model the dye transfer process. After the printing process was carried out according to the existing methodology (GOST 24356), the copy was dried and the optical density was measured. The thickness of the paint layer in the copy h_H was determined using the following formula:

$$h_H = \frac{M_1 - M_2}{S \cdot d} \cdot 10^4 \, [mkm], \tag{1}$$

where M_1 is the weight of the printing mold with paint before pressing, g; M_2 – weight of the printing die after pressing, g; S – area of printed copy, size 21 × 5 cm; d – aint density, 1 g/m^3 is accepted.

The obtained data (Table 3) show that there is an integral relationship between the structural parameters and optical parameters of printed materials. A linear relationship of the influence of the degree of gluing of the experimental paper on its swelling ability is observed. This situation is explained by the fact that when adhesives are added to the starting fiber materials, the adhesiveness of the fibers of the surface (that is, the top layer) increases, and thus the swelling ability of the base decreases due to the filling of hollow capillaries with adhesive solutions.

Table 3. **Results of modeling the dye transfer process**

Experience paper ≈ 150 g/m^2	M_1 The weight of the roller with paint applied to the press, g	M_2 Weight of the roller after pressing, g	$K_{tr.}$ Paint on paper, g (paint transfer)	Optical density	
				D	h
Sample № 1	129.249	128.954	0.295	2.06	28.09
Sample № 2	129.251	129.008	0.243	1.96	23.14
Sample № 3	129.257	129.018	0.239	1.93	22.76
Sample № 4	129.250	129.049	0.201	1.75	19.14

In this case, a thin film is formed on the surface of the absorbent material. That is, the dye remains on the surface of the paper without penetrating the internal pores of the paper, and the optical density indicators have high values (sample papers № 2 and № 3).

According to the results of the study, when the thickness of the paint layer is increased from 19 to 28 μm, the optical density of copies changes from 1.75 to 2.06.

The purpose of this experiment was to conduct spectroscopic studies in order to evaluate the interaction of cotton cellulose and modified polyacrylonitrile fibers in multilayer papers. During the research, the interaction of fibers and the formation of chemical bonds were analyzed in composite materials obtained in variants with different proportions of cotton cellulose and modified polyacrylonitrile fibers. In the experiments, crushed nitron fiber and cotton cellulose were analyzed in an infrared spectrophotometer of Perkin Elmer (USA).

Also, during the research, samples of Flint Group K+E Novavit F 700 triad offset printing inks (CMYK) were subjected to spectroscopic analysis. In the analysis of Cyan printing ink, NH_2, OH-hydroxyl groups, CH_3-methyl groups, -CH_2-methylene groups, υ-valent vibrations of C=O carbonyl groups were observed in the region of 1 733.28 cm^{-1}. Similar results were observed for the rest of the triad dyes due to the almost identical characteristics of the printing ink pigments [13].

On the basis of the color scales of offset printing copies printed on sample № 3, spectroscopic analysis of printing of yellow and red dyes on paper was carried out. The analysis showed that in the interaction of air dye with sample paper № 3, there are no C=O carbonyl groups and υ -valence vibration in the area of 1 733.28 cm^{-1} obtained in the air dye itself. This indicates that the dye is reacting with sample paper № 3 and forming a bond. A spectroscopic study of the interaction of modified polyacrylonitrile fiber waste with cotton cellulose showed that modified polyacrylonitrile waste interacts well with cotton cellulose in the process of paper production and serves to obtain papers with required strength indicators. Based on research, it can be concluded that the addition of modified polyacrylonitrile fiber waste to the composition of cotton cellulose in paper production helps to save cotton cellulose and obtain papers suitable for the production of packaging products [14] (Figures 1, 2). As a result of the research of nitron fiber according to this methodology, the following results were obtained: CH_3-methyl groups, -CH_2-methylene groups and -CH-υ-valent vibration were detected in nitron fiber in the region of 2 943.06 cm^{-1}. γ-valent vibrations with C=N double bond and C=N triplet were observed in the 2 245.42 cm^{-1} region.

υ-valence vibrations of C=O carbonyl groups were observed in the region of 1 736.83 cm^{-1}. δ-deformation vibrations of methyl, methylene groups were observed in 1 252.27 cm^{-1} fields. Spectroscopic analysis of the cotton cellulose sample shows the following: CH_3-methyl groups in the 2 917.24 cm^{-1}

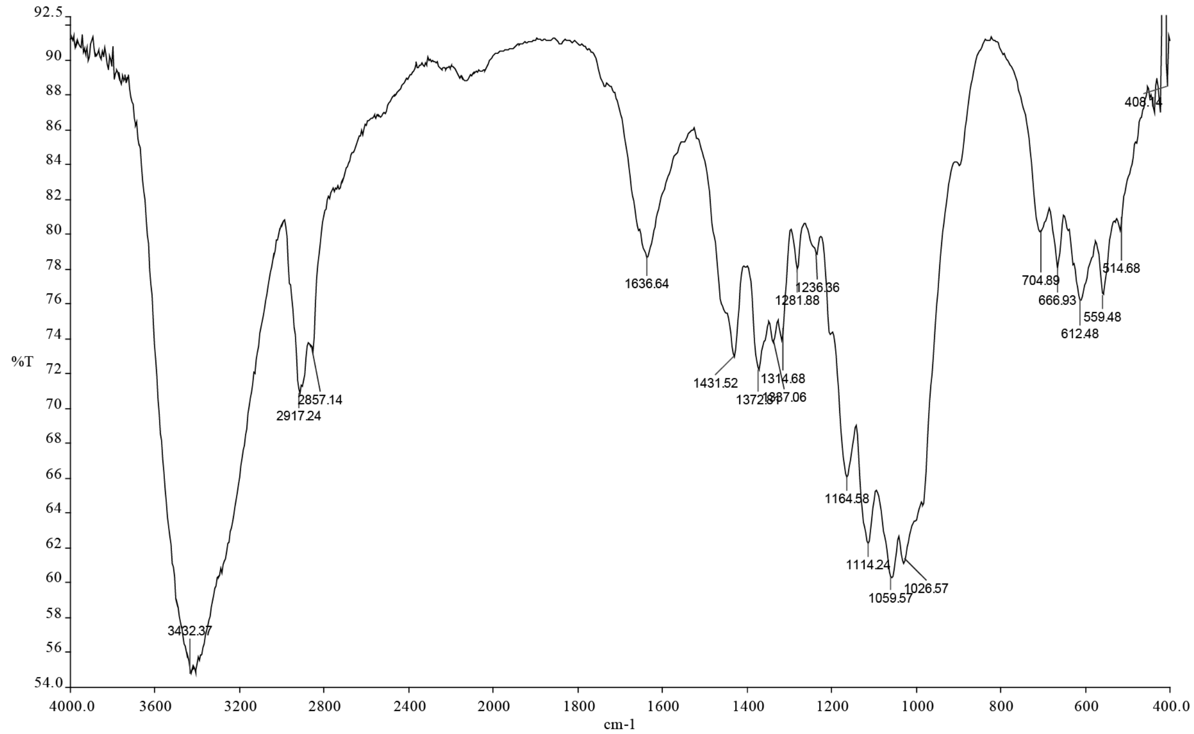

Fig. 1. Spectroscopic analysis of cotton cellulose

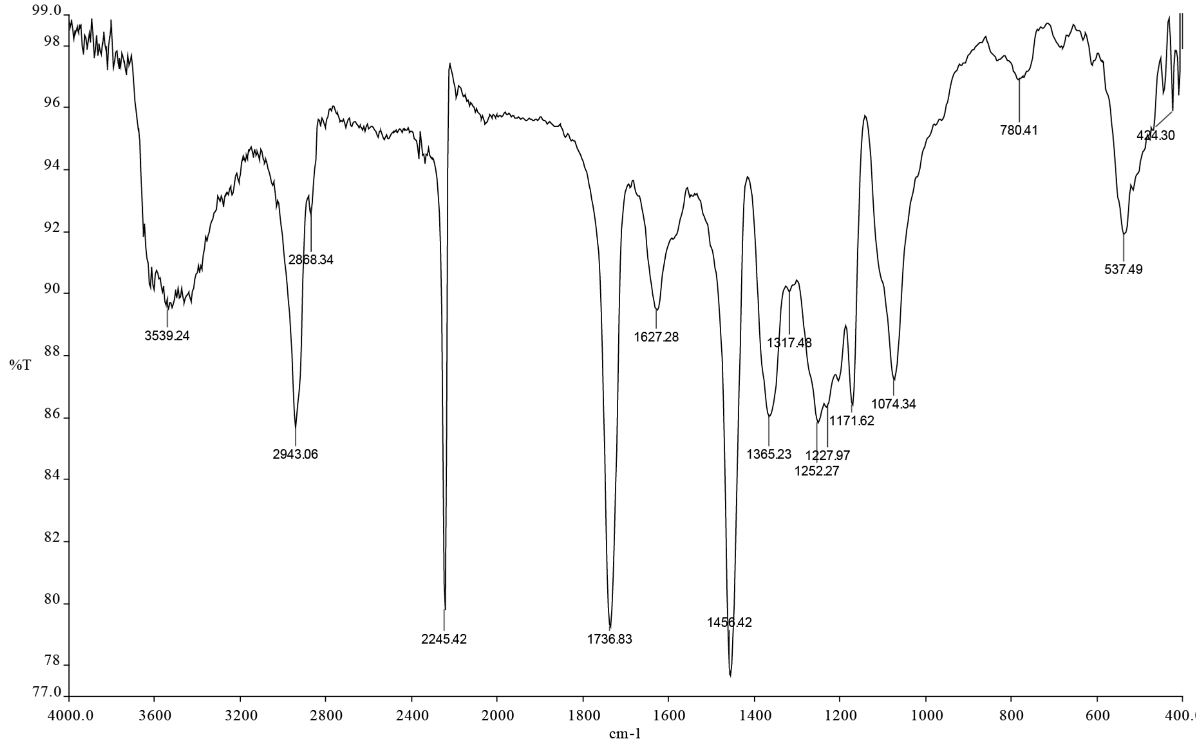

Fig. 2. Spectroscopic analysis of modified polyacrylonitrile

area, -CH_2-methylene groups and -CH-υ-valent vibration, OH-hydroxyl groups and γ-valent vibration in the 3 432.37 cm^{-1} area , OH-hydroxyl, CH_3-methyl, CH_2-methylene groups and δ-deformation vibrations were detected in the region of 3 432.37 cm^{-1}. An experimental paper sample with 80 % cotton cellulose and 20 % modified polyacrylonitrile fiber waste was subjected to spectroscopic analysis and compared with the results of spectroscopic analysis of pure cellulose and nitrone in order to determine the interaction between cotton and modified polyacrylonitrile fibers (Figure 3).

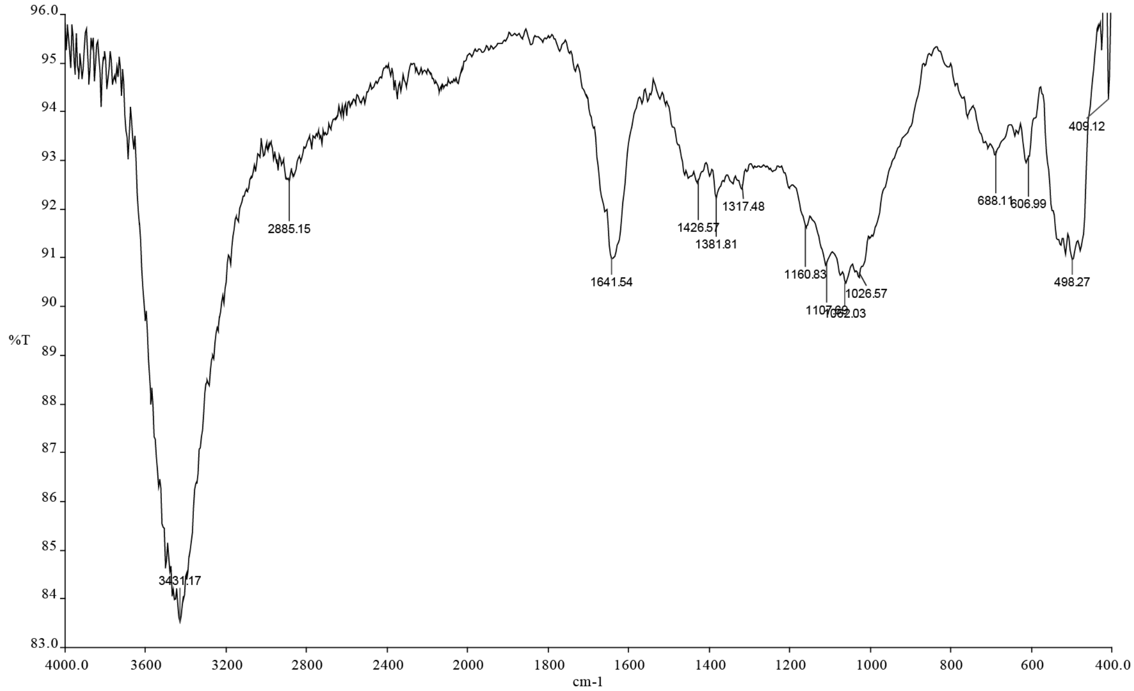

Fig. 3. IR Spectroscopic Analysis of Dye Reaction of Paper with 20 % Modified Polyacrylonitrile and 80 % Cotton Cellulose

In this paper example, the C≡N triplet in the nitrone fiber spectrum or the y-valence group in the S=N 2 245.42 cm^{-1} region and the δ-deformation vibration frequency in the nitrone fiber region C=O 1 736 cm^{-1} are also involved in the formation of a covalent bond. Experimental paper samples with 70 % cotton cellulose and 30 % modified polyacrylonitrile were subjected to spectroscopic analysis and it was found that the results were not significantly different from the results of papers with 80 % cotton cellulose and 20 % modified polyacrylonitrile (Figure 4).

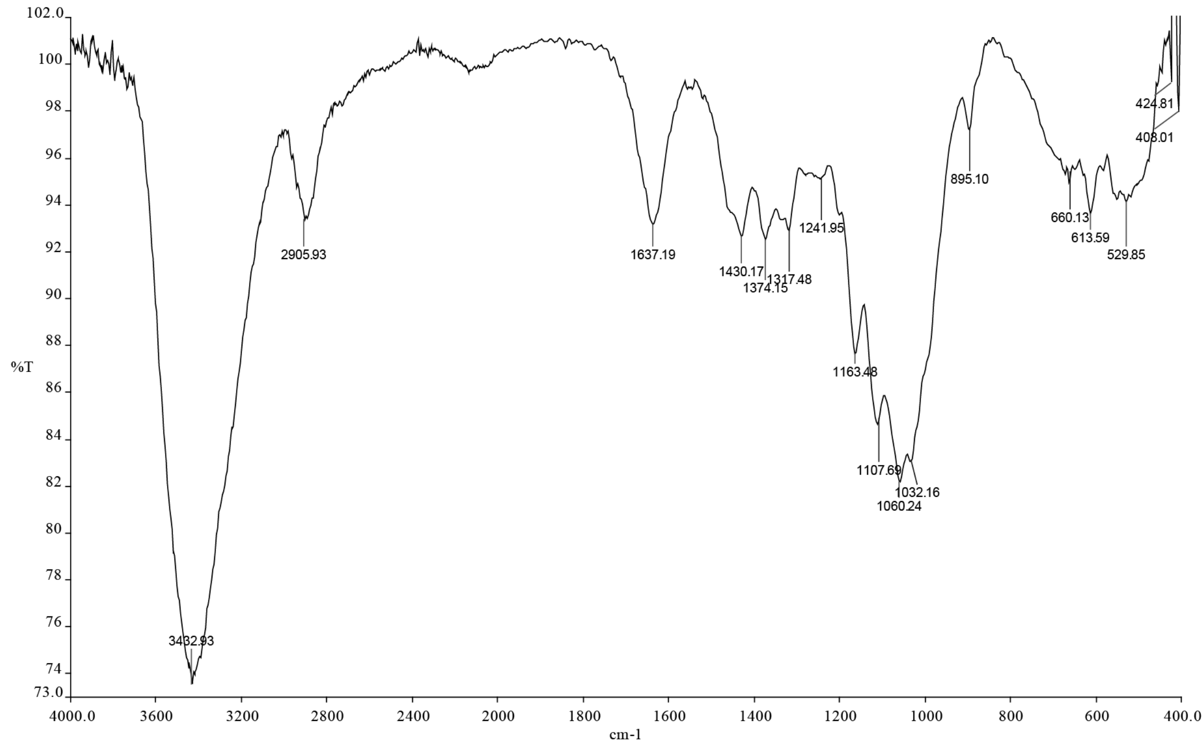

Fig. 4. IR Spectroscopic Analysis of Dye Reaction of Paper with 30 % Modified Polyacrylonitrile and 70 % Cotton Cellulose

The results of spectroscopic analysis of multi-layered papers with the upper part made of cotton cellulose and modified polyacrylonitrile mixture, and the lower part of waste paper were also similar to the results of paper sample № 2.

In this paper sample, there is no υ -valence vibration related to C≡N triplet or C=N group in the spectrum of modified polyacrylonitrile. It can be concluded that it is involved in covalent bond formation. In modified polyacrylonitrile, there is no frequency of d-deformational vibrations belonging to the C=O 1 736 cm^{-1} region, which is also involved in the formation of a covalent bond.

Conclusions. From the performed spectroscopic studies, it can be concluded that in the composite papers obtained because of cotton cellulose and modified polyacrylonitrile, fibers form cross-links. As a result, the upper layer will have the necessary strength to perform the printing process at a high quality level [14].

The types of papers used in the printing industry for packaging products and their interaction with paint are very relevant today. The quality of paper and dyes arriving at the enterprise and their interactions must be constantly monitored. Therefore, it is important to research the effect of new types of paper and cardboard recommended for printing on packaging products in the printing industry and to scientifically justify the results.In order to ensure the high-quality reproduction of color images in the copy, it is necessary to study the color coordinates and color coverage parameters of the copies obtained by the offset printing method.

The assessment of the compliance of the product quality level with the requirements of the state standard was carried out using the technical conditions of UzSSt 1066:2005 “Offset paper used for printing” as a base sample.The analysis of the obtained results showed that the breaking strength of paper depends not on the strength of individual components, but on the strength of the paper structure formed during the paper production process. Sample paper № 2 and № 3 have high mechanical strength indicators. This fact is explained by the fact that these samples have an optimally balanced composition of fibers, which ensures maximum inter-fiber coupling.The lower value of strength indicators for paper samples № 4 is descriptive, which is explained by the maximum amount of secondary waste fibers in the fiber composition. This situation indicates that a large amount of waste has been incorporated into the fibrous base as a cheaper substitute for cellulose fibers.

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