

Summary of the main results and scientific contributions

from the scientific works of

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presented for participation in a competition for the academic position of "Associate Professor" in the scientific specialty 5.10. Chemical technologies (Technology, mechanization and automation of the pulp and paper industry), announced by UCTM and published in the State Gazette, issue 67 of 13.08.2021.

Since 2008 I have been working as an assistant professor at the Department of Pulp, Paper and Printing art at the University of Chemical Technology and Metallurgy (UCTM) in Sofia, where my teaching and research activities are mainly in studying the processes in the chemical technology of paper and packaging production. Even as a student, I was very interested in studying the methods and technologies for the production of paper and cardboard and the processes of their transformation into finished products with a widely applied range. Subsequently, my education and personal research interests led me to study, already 14 years, the relationship between the type and quantity of paper components - different in nature primary and secondary fibrous materials, fillers and various chemical additives - in order to optimize their influence on the properties of the paper suspension, improvement of the technological processes and optimization of the consumption of chemical additives for obtaining the necessary balanced technological and consumer properties of the papers, cardboards and produced packages.

After granting the ERA Fellowship Program of the Federal Ministry of Education and Research of Germany in 2016, I had the opportunity to participate in the preparation and implementation of several research projects related to the recycling of polymer waste materials and their reinforcement with cellulose fibers, with the support of Prof. Michael Herzog and his team from the University of Applied Sciences, Wildau, Germany. Over the next three years under the Erasmus + program, I lectured at the same university on "Special Types of Paper", and subsequently received an invitation to lecture at the "1st International Teachers' Week in Wildau", Germany - 2020. As a result of this inherited long-term cooperation between the two universities and within the project 01DS19023 Bridge2ERA I organized a seminar "New polymer systems" at UCTM with the participation of specialists in the field.

Summarized data on my scientific, teaching-methodological and scientifically-applied contributions are presented in Table 1.

The current scientific contributions report was made on the basis of 50 publications, 21 of which are in scientific journals indexed and referenced in world databases (14 of them with awarded IF and/or SJR), and 29 are in no referenced scientific journals with reviewers (6 of them international). A total of 29 citations of the entire candidate's works have been noticed so far. According to the publicly available information in the Scopus database, the Hirsch index (h-index) is 1.

The accumulated knowledge and experience give me the opportunity to present my application for participation in the competition for the academic position of "Associate Professor" in the scientific specialty 5.10. Chemical Technologies (Technology, Mechanization and

Automation of the Pulp and Paper Industry), announced by UCTM and published in the State Gazette, issue 67 of 13.08.2021, and its successful passage will enable me and the colleagues I work with to continue to be in favor of the development of scientific activities at the University and our students.

Table 1. Indicators for scientific, teaching-methodological and scientifically-applied contributions

Scientific indicators	Publications, presented for participation in a competition for Associate Professor		Citations			University textbook		
	Refereed to global databases (from them with IF and SJR)	Non-refereed scientific, specialized publications with reviewers (from them international)	In referenced journals or in monographs and collective volumes	In monographs and collective volumes with scientific review	In non-refereed journals with scientific review	1		
	21 (14)	29 (6)	12	6	11			
Teaching indicators	Възложени лекционни курсове					Defended graduates		
	Total	Bachelors		Master's		Total	Bachelors	Master's
		Full time	Part time	Full time	Part-time			
18	4	4	5	5	23	17	6	
Scientific-applied indicators	Participation in a scientific or educational project		Management of an international scientific or educational project			Project management under contracts with SRS at UCTM		
	national	international	1			12		
	1	5						

The topic of the work, in the period after the PhD defense and the current moment, is divided into several scientific areas:

1. Investigation on the interdependences between the type of fibrous raw materials, processing methods and the properties of the papers obtained from them. Optimizing the recycling processes of fiber raw materials and improving their sheet-forming properties.
2. Study on the interdependences between chemical additives in paper production and their influence on the properties of paper. Optimizing the processes of dyeing, sizing and retention.
3. Investigations for optimizing the multifunctional properties of different types of packaging materials.
4. Investigation on the properties of corrugated cardboard for optimizing the processes of its obtaining and processing.
5. Others.

1. Investigation on the interdependences between the type of fibrous raw materials, processing methods and the properties of the papers obtained from them. Optimizing the recycling processes of fiber raw materials and improving their sheet-forming properties.

1.1. Investigation on the interdependencies between the type of source fibrous materials, processing methods and the properties of the obtained papers.

Paper like any physical material is characterized by a complex of properties that determine its reaction to various influences. The properties of the paper depend on the properties of the fiber raw materials, their morphological structure and chemical composition, the degree and nature of beating, the presence of fillers, sizing agents and other chemical additives, as well as the technological conditions of the production. Each type of paper is characterized by a certain combination and level of quality indicators due to the specific conditions under which it is used.

In order to optimize the energy-intensive beating process of fibrous materials, a study was performed [4_7] to determine the influence of a constant magnetic field (0.1T) on the behavior of the paper suspension and the strength of the obtained paper samples of bleached softwood and hardwood pulp. The magnetic treatment of the fibrous suspension with a concentration of 0.2% was carried out at a flow rate of 0.6-0.8 m/s with five and eight times passing through the magnetic field.

The proposed method for the magnetic treatment of bleached pulp from pine and acacia wood before beating is a suitable method for accelerating the beating time (to achieve a beating degree of 30 ° SR) by 4 minutes for pine pulp and 3 minutes for acacia pulp. The magnetic treatment of cellulose suspensions before beating improves the structure of the paper sheet, causes rearrangement of the fibers, which leads to increased strength of the obtained paper samples. For both types of cellulose, a quintuple passing is sufficient to achieve optimal strength.

The results describing the interdependencies between the type of fiber raw materials, the magnetic treatment before beating and the properties of the obtained papers have a scientific-applied character and are important for paper producers, as the permanent magnet used can be easily installed on any pipeline for transport of paper suspension before the beating equipment. The processing parameters used correspond to those in practice and the established effects of processing are most likely comparable for all bleached coniferous and deciduous pulps used for the production of paper for writing, drawing, painting, printing, documents and more.

Thoroughgoing studies have been conducted [7_9; 8_6] in order to investigate the relationship between the composition and the nature of the fiber raw materials of different types of paper (writing and printing paper, newsprint, wrapping paper, 1940s paper and five different types of paper for making labels for wine) and its properties in view of the specifics of its purpose. A comprehensive microscopic analysis was performed to determine the composition of the paper and a number of experimental studies were performed to establish its relationship with its properties by purpose.

After laboratory determination of the main properties of the used papers, an analysis of the obtained results was made and the main limits of structural-dimensional, capillary-hygroscopic, physico-mechanical and optical properties were determined. Of particular importance for the manufacturers of packaging and labels, as well as for the awareness of the designers working in this field, are the specifics of these papers, influencing the printability of the papers, allowing the correct choice of printing technology and finishing processes. In addition to the analysis of the relationship between the composition and the properties of the papers, specially modeled printing

samples were made, printed with different types of printing (offset UV, flexo UV, screen, cold foil, hot foil, silk foil) and finishing (stamping, laser cutting, laser engraving) techniques in the conditions of Rotoprint printing house, Ravno Pole. Based on the obtained results and the evaluation of the quality of the printed samples, ten new designer labels for wine were printed, and conclusions were made about the relationship between the type of fibrous material, the properties of the papers and their printability.

The dependencies between the type of the fiber raw material in the paper and the appropriate printing and finishing techniques are defined:

- Pulp paper made of 100% natural cotton with high porosity and low strength can be used for the production of wine labels with a clear design through various printing techniques without finishing processes.

- 100% natural bleached cellulose paper from coniferous and deciduous wood species with high porosity and strength could be suitable for the production of wine labels through various printing techniques with a variety of finishing processes.

- Paper with different fiber composition, including more than three types of wood materials, also cotton fibers, with high-density and low porosity with medium hydrophobicity could be suitable for the production of wine labels through almost all printing processes and finishing techniques.

- Paper with a different fiber composition, including more than three wood materials, also cotton fibers, low porosity and water-absorbing properties could be suitable for the production of wine labels with a clean design, which include mainly finishing rather than printed processes.

- Deeply colored paper with a different fiber composition, including more than three wood materials, also cotton fibers with high density, low-porosity and high water-absorbing could be suitable for the production of wine labels, which include mainly finishing rather than printing processes.

- Papers with a highly developed surface macrostructure (produced by marking felt) are characterized by a risk of dust and lint during printing and finishing processes.

In the specialized literature with extreme rarity could be found studies characterizing the relationship between the type of the wood raw type of cellulose, which are part of the paper and its printability. Due to the extensiveness of the performed analyzes, the results of the work in this direction are not only with applied contribution, but also have scientific value.

The laboratory tests and industrial experiments conducted in the printing house are comprehensive and the specially modeled printing samples used with extensive printing technologies and finishing techniques have a significant practical application. Based on the characterization of the relationship fibrous composition - paper properties - printability, with great accuracy could be made predictions about the applicability of different printing and finishing processes in different types of paper for high quality labels and the effect of their application.

The applicability of the described dependencies allows saving materials and time for preliminary printing samples in the development of new designs of labels and other printing products.

1.2. Investigation of the kinetic regularities between the type of the source fibrous materials and the aging of the paper.

Specific external sign of paper aging is the decrease in the degree of whiteness and deterioration of the physical and mechanical properties of the paper. Accelerated artificial thermal aging is performed to study the resulting changes. The aging result is primarily related to the presence of carbonyl groups formed as a result of the oxidation of the hydroxyl groups at the second and third carbon atoms in the elemental unit of the cellulose macromolecule and the presence of both aldehyde and carboxyl groups in the cellulose materials. The decrease in the degree of whiteness of the paper could be related to the presence of lignin, hemicelluloses, the presence of metals and the type of sizing.

Paper as an elastic, plastic and capillary porous material, which breaks down rapidly at increased temperatures. The degree of change in the paper depends not only on the temperature but also on the duration of the impact. In order to study the kinetics of aging in coated printing paper, artificial thermal aging is performed at three different temperatures - 90, 105 and 120 ° C for 48 hours [7_7]. In order to study the kinetics of the process, a certain degree of whiteness was determined. The paper used is for the covers of books and is highly exposed to external influences. The basic weight of coated paper is 128 g/m². Microscopic analysis of the composition of the paper revealed that it consisted of secondary fibrous material of bleached pulp from coniferous spruce wood and bleached cellulose from deciduous poplar wood.

The kinetics of the process is described by an exponential kinetic equation valid for a heterogeneous process occurring on uniformly inhomogeneous surfaces. The initial and current speed of the process are determined. They have been found to decrease with increasing of the process rate. The constant rate of the reaction is also calculated. The temperature dependence of the velocity was also traced and the values of the activation energy and the pre-exponential factor in the Arrhenius equation were calculated.

In addition to the classical methods for analysis and calculation of the kinetic dependences, computer-aided studies have been performed [7_8], using simulation models (drying model, pyrolysis model, homogeneous reaction model, coal oxidation and gasification model) to determine the processes in burning eucalyptus wood in a biomass furnace. The modeling was validated by comparison with the measured laboratory data. A good correspondence has been achieved between the model and the measured data.

The research conducted describing the kinetic dependences of aging of coated printing paper has a scientific contribution. It is confirmed that the current speed of the process of artificial thermal aging of the paper decreases with increasing the degree of the process and increases with increasing the temperature.

The increase of the activating energy and the pre-exponential multiplier with the increase of the degree of the process α is connected in a general linear dependence, known as the “compensatory effect”. The conducted research are been important in controlling the aging process of books.

1.3. Optimizing the recycling processes of fiber materials and improving their sheet-forming properties

The development of the pulp and paper industry in recent years is associated with solving a number of environmental, energy and raw material problems. Recycled waste paper is one of the

most important raw materials for the paper industry. It represents about 50% of the fibrous raw materials used in the production of paper and cardboard. Characteristic of the secondary fibrous materials (SFM) is the destruction of the cell walls, in which a fine fraction is released, which strongly swells and turns into a gel-like form. It causes water retention, slowing down the drainage, slowing down the drying and increasing the chemicals consumption.

One of the perspective and ecological methods for improving the sheet-forming properties of SFM and increasing the ability to re-use them in paper production is their modification through the use of enzyme products. The mechanism of their action is expressed in the hydrolysis of the gel-like form of the fibers.

In a series of studies [8_11; 7_2; 8_24] with different origin of SFM (from waste corrugated paper, offset printing paper and a general group of waste paper) aiming to determine the effect of enzymes (cellulase, lipase, amylase and xylanase) on drainage, in flotation and strength of the obtained paper samples to generalized assessment of their sheet-forming properties have been done.

The results obtained for the secondary fiber materials after treatment with cellulase enzyme [8_11] at a concentration of 6-10%, temperature 60 ° C, pH = 4-7 and enzyme consumption 0.05-0.5%, confirm the positive effect - improving drainage by 45% with minimal fiber loss and tensile strength with about 15% and slightly reducing the tear index. It also has an effect on SFM from the general group of papers, which is characterized by a high content of residual fillers, sizing agents and chemical pulp, which requires the use of a higher enzyme consumption.

In the study of deinking of waste paper with offset printing by flotation [7_2; 8_24] and the use of various enzymes - lipase, cellulase, amylase, xylanase and surfactants were carried out stages of fiber defibering in laboratory hydropulper, additional defibering in a disintegrator at a concentration of 2 %, flotation with enzymes with a consumption of 0.1-0.3 % in a flotation cell and obtaining paper samples. In all samples there is an increase in the deinking ability, with an increase in the concentration of the corresponding enzyme. This is most significantly seen with the enzymes lipase and xylanase. They have best deinking ability, which is a combination of all enzymes due to the synergistic effect between the enzymes. The physico-mechanical and optical properties of the deinked secondary fibrous material by enzymatic flotation were studied and compared. The results show that when using different enzymes, the physico-mechanical parameters do not change significantly as the obtained samples by flotation with the enzyme amylase at a concentration of 0.1% have the best strength properties. The study on the optical parameters of the paper samples shows that the highest whiteness values are obtained with a combination of the four enzymes in flotation.

The optimal enzymes consumption depends on the type of the waste fibrous material and is higher in the presence of fillers and other additives. The resulting SFM could be successfully used in the composition of various types of paper, as accelerated drainage is a prerequisite for easier drying of the paper web and helps to reduce heat consumption to increase the capacity of the paper machine.

In the study on the possibilities for prevention of degradation of the starch used in the production of paper for corrugated cardboard (CCB), in the process of recycling [8_3], a zinc-based product (zinc sulphate 28-30%, zinc chloride $\leq 0.58\%$) was used, which inhibits the amylase enzyme. All experiments were performed at zero and 24 hours of downtime of the paper suspension. The raw material used is SFM from the production of a test liner for CCB, supplied by

DS Smith Bulgaria SA. The defibering is performed under laboratory conditions in a hydropulper to a refining degree of 35 °SR. The additive is used at a consumption of 0.5% to 2%. The amylase enzyme inhibitor prevents the enzymatic degradation of the starch polymer and the results of the analysis of the paper suspension show a positive effect of the enzyme inhibitor on the effect of dewatering and turbidity of the white waters. The investigated strength and deformation properties of the obtained paper samples are constant before and after 24 hours of downtime. The result of the starch concentration in the white waters is in the range of 0.05% even after 24 hours of downtime of the paper suspension.

Nowadays, manufacturers are focused on increasing the sustainability of processes, reducing the basic weight of the paper and increased requirements for environmental protection. One of the possibilities for process optimization is the use of sludge from the wastewater treatment system, as they require additional costs for dewatering and compaction before final disposal.

The focus in this [7_11] study was exploring the possibility of sludge usage in paper production in order to decrease fiber losses. The main purpose was to investigate the effect of the sludge over the main mechanical properties of the packaging paper, produced with different composition. The potential issues in the real production of DS Smith Bulgaria SA were also taken into account.

Two methods have been proposed for the preparation of paper samples, consisting of SFM and a different volume of sludge (15% and 30%) from the two basic precipitation points - DAF (Dissolved Air Flotation) and ETP (Effluent Treatment Plant). The sludge was added to paper suspensions taken from the three-point production line - after the hydropulper, after screening and from the machine tank. Both investigated DAF and ETP sludge have positive effect over the examined dynamic packaging paper parameters (CMT and SCT) when the sludge is added in consumption of 15% before or after the chemical additives and it consist of more long fibers. Due to the darker colour of the ETP sludge it would require to be used only in the middle layer for the testliners. Further investigations are required to observe if a synergy effect could appear of using both DAF and ETP sludge together in one flow as in real production in order to be implemented in machine trails. Next step will be production test where the focus will be on wet-web strength and the effect on the sizing of the paper.

The extensive research conducted on the effect of the enzymatic treatment of SFM and the use of production sludge in the composition of the paper is innovative and has a proven scientific and applied contribution. All studies have positive results and have been developed with the participation of students and PhD students at the Department who work in the respective companies. The obtained results have been taken into account, as some of them have been taken out to optimize the production processes in DS Smith Bulgaria SA and are applicable to all manufactures for the production of test liners and fluting papers from secondary fibrous material.

2. Study on the interdependences between chemical additives in paper production and their influence on the properties of paper. Optimizing the processes of dyeing, sizing and retention.

The variety of paper applications achieved so far is only possible through the development and the use of various chemical additives (CA). At the same time, CA have a significant effect on the increased use of raw materials, energy and capital savings. This ensures an environmentally friendly and efficient paper production. There are two main highlights that are being addressed to and why the use of 3% chemical excipients (CA) is mandatory. Chemical additives that improve

the quality of the paper and ensure the achievement of certain of its properties (functional CA), to ensure whiteness/color, hydrophobicity, strength, barrier properties, etc. Some of the optical brighteners have other applications besides the classic tinting of the paper and are very often used for special types of paper such as sensors and indicators [7_4], different mineral fillers are used to improve the printing properties [8_19]. Chemical additives, which favor the course of the main technological processes in the production of paper (process CA), ensuring optimal productivity and environmental friendliness.

2.1. Investigation and optimization of dyeing processes with new reactive dyes

Due to the great rarity of research on the applicability of reactive dyes in paper production, a number of experiments were conducted [8_23; 4_5; 8_1; 8_2; 4_4] with new, laboratory-synthesized reactive dyes and a comparative analysis of their action was performed against reactive dyes available in practice. The dyeing was performed in order to obtain offset printing papers from primary fiber materials from bleached coniferous and deciduous pulps and their effect on the properties of paper suspensions (drainage, turbidity, conductivity, pH, color) and capillary, hygroscopic, mechanical and optical (before and after 72 hours of artificial thermal and light aging) properties. The experiments were performed in accordance with the conditions of real paper production with the corresponding CA (sizing agent alkyl ketone dimer (AKD) - 2%, filler natural calcium carbonate (CaCO_3) - 20% and modified polyacrylamide with cationic charge with consumption of 0.05% as retention additive). The consumption of the dyes is 0.2%, 0.4%, 0.6%.

According to the data on the scientific literature, the mechanism of retention of reactive dyes is through the formation of covalent dye-polymer bonds, for example, with the hydroxyl groups of cellulose. Experiments have shown that dyes containing a monochlorotriazine reactive group are able to react with cellulose fibers in the presence of alkalis to form a covalent bond between the dye and the fiber.

The both tested dyes are laboratory-synthesized red reactive dyes. The compounds are monoazo reactive dyes, the chromophore of which is an orange acid dye obtained by diazotization of amino acid C and subsequent coupling with I acid in a weakly alkaline medium. A reactive group (chlorine atom) is introduced into the chromophore by reacting the acid orange dye with cyanuric chloride to give a dichlorotriazine reactive dye. In the next step, by reacting the latter with 4-amino-2,2,6,6-tetramethylpiperidine or ammonia, monochlorotriazine reactive orange dyes were obtained. The fragment of tetramethylpiperidine in the molecule acts as a stabilizer and its introduction is made in order to increase the color resistance to light (photostability). Dyed paper should also have greater photostability based on the fact that dyed fibers (cotton and wool) and chemically colored polymers show high photostability.

It has been found out that the most suitable in terms of drainage capacity and turbidity of the white waters is the reactive dye 2 even at a low consumption of 0.2%, and in terms of all the properties of the obtained paper samples, best result is obtained again with reactive dye 2, but at 0.4% consumption, which proves the formation of a covalent bond. The two reactive dyes produce paper samples with stable and uniform coloring, with both dyes producing paper with similar color shades almost imperceptible to the human eye, characterized by stability in thermal aging.

During accelerated thermal aging, the color changes are smaller and smoother, while in light aging the color changes are larger and have more variations in the color parameters. The most variable color parameter during accelerated aging is the C^* chromaticity. During the thermal aging, the color characteristics of the dyed paper samples 1 are more stable over time, and those of dye 2

are more stable during light aging, demonstrating the positive effect of the presence of a stabilizing fragment in its molecule.

Due to the fact that reactive dyes require high electrolyte concentrations, a fixing agent (cationic chemical reagent) is used before adding the reactive dye to improve the interaction of the dye with the fibers and the fixing ability of the dye. Dyes present in wastewater would destroy the natural quality of the aquatic environment and may also cause harmful long-term health and environmental effects. Therefore, laboratory experiments have been performed [8_1; 8_2; 4_4] with three reactive dyes, both of which are laboratory-synthesized monochlorotriazine reactive orange and reactive red dyes containing a stabilizing fragment, and the other is a commercial product from Kemira's Levacell® range.

The reactive dye 2 used in the previous studies was compared with one commercial reactive red dye from the Kemira-Levacell® Neon Red 2B Levacell® range and a new synthesized dye 3. It was synthesized similarly to RD 1, where instead of amino C acid and I acid 2-aminobenzenesulfonic acid and H acid were used. The paper suspensions for the preparation of paper sheets were prepared in the following order of addition of the components: Cellulose - Fixing agent - Reactive dye - Sizing agent - Filler – Retention additive. A cationic polymeric fixative based on epichlorohydrin-dimethylamine copolymer with a consumption of 1% was used to fix the reactive dyes.

The established accelerated dewatering and increased retention due to the effect of flocculant and dyes usually also mean cleaner water in the paper mill. In the process of adding the reactive dyes to the paper suspensions, a covalent chemical bond is formed - dye-cellulose. This is the reason for capturing of part of the hydroxyl groups by the cellulose fibers, so that they are not able to form bonds with water. Therefore, the cellulose fibers are less hydrated and water passes more easily through the formed cellulose network. It was found out that the effect depends on the charge density of the dye - the higher the charge density, the greater the effect. The concentration of dyes in the white waters is negligibly small, as both laboratory synthesized reactive dyes gave practically pure white waters. The most suitable in terms of turbidity and conductivity of white waters is the reactive dye 3.

With the addition of the tested reactive dyes, the hydrophobicity increases, which saves on the sizing agent, and the tensile strength of the paper samples improves or remains unchanged. The positive effect of the tested reactive dyes on water absorption could be considered as a great advantage over other types of dyes used in the paper industry.

During the thermal aging, the colored paper samples with higher dye consumption are more stable over time, and the changes are smooth. While with accelerated light aging, the color changes are larger and have more variations in the parameters and after the 36th hour of aging the paper "burns".

Based on the used complex approach in studying the applicability of laboratory-synthesized reactive dyes for paper production, monochlorotriazine reactive orange and red dyes for dyeing paper for offset printing are proposed, which are of interest for industrial production. The approach used claims completeness and circumstantiality in characterizing the quality indicators of colored paper suspensions and paper samples. Research in this field has scientific value in terms of synthesis and applicability of monochlorotriazine reactive dyes with a stabilizing fragment in paper production. The effect on the clarification of the white waters

depends on the charge density of the dye - the higher the charge density, the greater the effect is.

For the first time, the reactive dyes consumption range for paper production is being determined and their resulting color coordinates are measured. The data for the color coordinates, before and after the conducted artificial thermal and light aging, could be used for analysis and prediction of color change during storage of publications in libraries and repositories of papers dyed with acid dyes.

2.2. Investigation and optimization of sizing processes to improve the barrier properties of papers

Sizing or giving hydrophobic properties to paper is an important and complex process in paper production. This type of chemical additives (CA) prevents or slows down the penetration of water [8_11; 8_28; 8_9], oils [8_26] and other liquids in the paper web and ensure the dimensional stability of the paper sheet. The most commonly used reagents in the neutral-alkaline conditions over the last 10 years are alkyl ketene dimers (AKD) and alkenyl succinic anhydrides (ASA). AKD is a dimer of ketene, with two alkyl chains derived from two fatty acids by dimerization of their acid chlorides. AKD is less reactive than ASA. It hydrolyzes more slowly than ASA, but sizing with it is not as fast as with ASA. The AKD emulsion is delivered to the paper manufacturer with a concentration of 5-15% and is stable for a period of several weeks to several months, depending on the storage conditions.

The degree of sizing with AKD increases with increasing the pH level from 6.5 to 8.5, with the optimal pH value being 7.5. ASA has a long hydrophobic residue (alkenyl) and hydrophilic groups (anhydride), which serve for orientation or fixation on the fibers. In this case, the fixation of the adhesive on the fibers is done by chemical reaction with the hydroxyl groups of the cellulose (esterification). ASA is highly reactive, which is why its anhydride groups react not only with cellulose but also with water to form by-products (dicarboxyl derivatives). These derivatives are not effective in terms of sizing, i.e. they do not size. For these reasons, ASA requires special conditions for its use as a sizing agent and cannot be supplied to paper mills as a ready-to-use additive. Immediately before use, the ASA is emulsified with a cationic agent.

Studies have been conducted [8_11; 8_28] to establish the effect of AKD type sizing agents on the properties of paper suspensions, finished paper and their stability during thermal aging. The experiments have been performed with bleached primary softwood and hardwood pulps to obtain colored offset printing papers and secondary fibrous material from corrugated production. In the first group of experiments, along with the hydrophobic additives, CA was added to the suspensions for dyeing, filling and retention. The drainage capacity, the dispersed substances and the turbidity of the suspensions were determined. The capillary-hygroscopic, physico-mechanical and optical properties were determined on the obtained paper samples.

It was found out that the effect on the studied properties is directly dependent on the amount of active substance in the sizing agent and its consumption. In addition to the expected hydrophobic effect, the tested sizing agents also show a retention effect (in relation to the filler, with an improvement of 10-13%, at a consumption of 0.5-1.5% and in relation to the dye, characterized by stability of the color after 72 hours thermal aging). This optimization of properties is essential for the sustainable development of paper production.

The effect of the sizing substances has been proven [8_9] - reduction of the penetration of various liquids in the paper, and in some cases a change in the mechanical strength, associated with

an increase in the bonding forces between the fibers in the paper sheet. ASA is used for sizing a copy papers, high-filled printing papers, kraftliner, testliner and other papers and cardboards based on secondary fibrous material, wrapping papers, as well as papers with thermomechanical pulp (newspaper), etc., but for paper production in Bulgaria is interested in sizing kraft paper for the production of paper for sacks. These papers are a specific type of paper for which it is essential to have high dynamic strength and elasticity, but also a certain hydrophobicity, due to the specifics of their application and the need to apply a printed image on the produced paper bags. Therefore, it is of scientific interest to specify the conditions for the use of an alkenyl succinic anhydride (ASA) sizing agent for sizing paper. The studies we carried out with fiber material of 100% unbleached sulphate softwood cellulose, with beating degree of 17 ° SR, taken from the production line of Mondi Stambolijski EAD.

A method for emulsification of sizing agent and starch has been proposed, and a significant amount of experiments have been performed to determine and optimize the ratio of sizing agent-starch and emulsification rate.

Paper samples have been prepared with composition and sequence of addition of chemicals from 100% unbleached sulphate coniferous cellulose - cationic starch - 0.3% - antidusting agent - 0.14% - ASA - 0.05; 0.1; 0.15; 0.2% - retention additive SiO₂ - 0.16% or modified polyacryl amide with cationic or anionic charge - 0.02%.

The degree of sizing was determined on all paper samples as Cobb₆₀ water absorption capacity and the main physical and mechanical parameters (resistance to tearing, bursting, tearing and double bending).

It was found out that the paper has the necessary hydrophobic properties, as optimal results are obtained by emulsification with ASA and Starch in a ratio of 1: 1, as the sizing agent does not affect or slightly improves the physical and mechanical properties of the paper for bags. Depending on the type of sizing paper, the consumption of ASA is in the range 0.05-0.15% of o.d.f.

The main tendency in the paper production for the last 5 years is the transition to surface application of CA both for hydrophobicity and for oil resistance and bactericidal properties. The advantages, besides economic, due to 100% utilization of the additives, are also ecological, reduce the pollution of circulating waters and reduce the used additives for purification.

In order to optimize the surface application processes, studies were performed with three additives on two different types of paper (bleached and unbleached cellulose) for food packaging. Two aqueous copolymers of styrene butadiene and an aqueous dispersion of perfluoro-alkyl acid were used to obtain oil-barrier paper with respect to oil resistance [8_26]. The best results in terms of oil and water resistance show the copolymer of styrene butadiene at a relatively low coating weight.

The results on the research and optimization of sizing processes to improve the barrier properties of papers have a significant scientific contribution due to its comprehensiveness, in terms of emulsification rate and ratio in emulsification of sizing agent and starch, as there are currently a limited number of studies conducted by scientific teams independent of the manufacturing companies characterizing the emulsification processes of these two chemical additives. Investigations could serve researchers and papermakers to quickly and successfully select the type, amount and emulsification of the emulsifier ASA with starch, as they also provide clear guidelines for the right combinations of fibrous materials and suitable sizing agents.

2.3. Investigation and optimization of retention and drainage processes in paper production. Improving the properties of paper suspensions and the clarity of the white waters.

Water is an indispensable component in the production of paper. Its use is inextricably linked to the protection of the natural environment. Therefore, the rational water cycle is one of the important problems in any paper mill. In this aspect, the main task is the effective treatment of circulating water with a view to their reuse and reduction of water consumption.

There are three methods for industrial water treatment: flotation, filtration and sedimentation. All of them provide for mechanical separation of the dispersed substances. In fact, fine particles of fibers, fillers and other substances, some of which are close in size and properties to colloids, are difficult to separate by purely mechanical means. With the increased use of secondary fibrous materials that are part of the paper eco-cycle, the problem is enhanced. This imposes the need for the use and investigation [8_7; 4_3; 8_12; 4_2] of chemical agents causing coagulation and flocculation. As a result of their action, agglomerates are formed, which are more easily separated by precipitation, flotation or filtration.

The precipitation of white waters [8_7], obtained in the production of paper from 100% secondary fibrous material in the presence of cationic flocculants and different pH, provided with coagulant aluminum sulfate, have been studied. The white waters are taken from the production of wrapping paper from 100% mixed waste paper from the paper machine of NKF “Iskar”-Sofia with content of dispersed substances - 1.1 g/l, dry content - 2.3 g/l, pH = 6.8, turbidity - 978 NTU units and electrical conductivity - 1142 μ S. Flocculants are synthetic polymers, cationic acrylamide copolymers with different molecular weights and charges. This explains their high saturation with colloidal dissolved "interfering substances", which makes them difficult to clean.

The experiments were performed according to the author's methodology with samples of 1 l of white water placed in a graduated settling tank. To adjust the pH of the system, a solution of coagulant - aluminum sulfate with a concentration of 100 g/l was added.

Of the five cationic flocculants studied, the action of the cationic polyacrylamide with medium charge and average molecular weight is the best in terms of the effect on precipitation, as the reduction is on average by 2 to 5 times and the turbidity of the clarified waters is reduced by about 2 times. The results show that for effective purification it is necessary to lower the pH by adding a coagulant, which helps to reduce the thickness of the electric double layer of colloidal particles, as a result of which their negative charge is reduced and they have the ability to bind to each other by means of Vander-Waals binding forces. The presence of flocculants provides their additional consolidation.

In the study of the drainage capacity of paper suspensions of 100% unbleached sulphate coniferous cellulose [4_3], taken from the technological flow of Mondi Stambolijski AD, the action of an anionic flocculant was evaluated at three consumptions (0.01; 0.02; 0.03%) without and with magnetic field treatment of constant intensity. On the obtained paper suspensions were determined: flocculation volume - V, ml and sedimentation index - SI, % by author's method; drainage capacity (SR) – T_{700} , s; retention capacity (Britt) - R, %, and the electrical conductivity and turbidity (NTU) were determined on the white waters.

As the consumption of the retention additive increases, the SI values increase both with and without magnetic treatment, and the flocculation volume decreases. The effect of the magnetic treatment of the paper suspension on these indicators is the destruction of the hydrogen bridges in the water. The resulting flocs settle more easily because the water is more fluid and leaves the

agglomerates more easily. The result is smaller and tighter flocs. The effect is greater the higher the consumption of the retention additive, due to the increased charge of the system.

The positive effect of the magnetic treatment is also confirmed by the results for the overall retention. In the dynamic drainage of the suspensions of the DDJ apparatus, with the increase of the consumption of the retention additive the retention improves, and decrease with increase the shear forces caused by the increase of the revolutions of the apparatus. The greatest effect has the magnetic treatment of a suspension containing 0.01% retention additive at 1000 rpm. This consumption is quite sufficient for good retention and drainage, which means that the "paper suspension" system has reached optimal values of its characteristics, which are further improved by the magnetic treatment.

The characteristics of the white waters confirm the effect of the magnetic treatment. The values for turbidity and electrical conductivity change in the direction showing the clarification of the waters with increasing consumption of the retention additive and with the magnetic treatment. The most noticeable is the improvement of these indicators in suspensions without a retention additive, which is due to the lighter system. The addition of an anionic copolymer obviously requires a higher intensity magnetic field.

The conclusions made from this study show the positive impact of magnetic treatment of fluids on the course of technological processes in paper production and on the properties of paper. Magnetic treatment could not replace the use of suitable chemical additives, but it could increase their effectiveness, leading to a reduction in their cost. It is technologically convenient, completely environmentally friendly and requires minimal investment and operating costs, which is a prerequisite for the actual application of this method in practice.

Also with a great importance from an ecological point of view is the production of wood fiber boards, where the purity of the wastewater is essential, for which the action of flocculants with different molecular weight and charge on the filtering ability [8_12] of wastewater is analyzed. Nine low to high molecular weight flocculants have been used to perform the studies. Seven of them have a positive charge in the range of 0.8-2 meV and one with a negative charge (1.2 meV) and one neutral.

Of all the flocculants used, the flocculant, which has an average molecular weight and a relatively higher cationic charge, has the best effect. Nonionic and anionic polymers do not have enough effect on the drainage capacity, the charge of the used flocculants has the greatest influence. In specific studies, a cationic flocculant with a higher charge has twice the effect on the drainage capacity than one with the same molecular weight but a lower charge.

To improve the strength properties of dry papers [4_1], natural and synthetic organic substances with a hydrophilic character are used, which have a pronounced affinity for cellulose fibers. As a result of their presence, the bonding forces increase and the strength and structure of the paper improve. Lower molecular weight anionic and cationic polyacrylamides play such a role. Cationic PAA contains amine groups through which it binds well to the fibers, flocculates less and helps to obtain a homogeneous structure.

Secondary fibrous material (SFM), obtained from newsprint paper and neutral sized paper for offset printing in a ratio of 1:1, was used for the research. After obtaining colored paper samples with a basic weight of 70 g/m², with a composition of fibrous material, dye, sizing agent, filler and cationic low molecular weight polyacrylamide (DSR) were determined water absorption by Cobb₆₀, indices of rupture, cracking and tearing, filler content and artificial thermal aging at a

temperature of 105 ° C for 72 hours have been carried out, and before and after aging color parameters were determined. L^* , a^* , b^* and the color difference $\Delta E = \sqrt{\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2}}$ is determined. The consumption of sizing agent (1%, 2% and 3%) and polyacrylamide for dry strength (0.1%; 0.2%; 0.3%) were varied.

It was found out that with increasing the amount of sizing agent from 1-3% at DSR-const = 0.1% increases the hydrophobicity of the samples from 55 to 19 g/m². By increasing the consumption of DSR from 0.1% to 0.3% in AKD-const further hydrophobicity improves, the content of the mineral component increases, and the role of DSR is flocculating with retention action, improving the retention of short fibers and fillers.

The action of cationic DSR as a binder (a means of improving the strength in the dry state) stands out not only in determining the physico-mechanical properties, the index of tear and burst, but also in the color parameter L^* . They increase with increasing the amount of the polymer. The higher the content of the sizing agent has, a positive effect on the change of these indicators have been observed. The bonding forces increase and they compensate for the negative impact of the mineral component. The denser structure also determines the lower tear resistance and it decreases with increasing the DSR consumption, but its values are higher at higher AKD consumption. The results of the studies show that in the presence of secondary fibrous material, including mechanical fiber material, softwood and hardwood pulp and filler, a highly filled paper with a mineral component content of 18.5% and very good hydrophobicity - 20 g/m² and sufficient strength when using 2% AKD and 0.2% DSR is obtained.

As a result of the thermal aging, a change in the color parameters is established. The paper becomes darker due to the mechanical pulp, which changes more under these conditions. The color difference ΔE decreases with increasing the amount of anionic DSR and AKD as a result of the increased filler content. The change in ΔE shows that regardless of the fibrous material, the presence of CaCO₃ filler and the neutral-alkaline environment in the production of papers are a favorable factor for less paper aging and serve as a buffer for the products obtained by the oxidative action of air on paper. ΔE changes in the range (1.2-1.58).

Of significant scientific and applied character are the proposed author's methods for determining the rate of precipitation of particles in paper suspensions and the flocculation capacity of chemical additives in paper production, which are published in the co-authored manual - Assoc. Prof. Dr. Nadezhda Ivanova, Assoc. Prof. Dr. Eng. Siyka Bencheva, Dr. Eng. Dimitrina Todorova, "Handbook for exercises in chemistry, technology and properties of paper", UCTM, Sofia, 2009 - in 2.2.1.2. Determination of kaolin particle size, "Particle precipitation rate (v, m / s)" - p.7 and 2.6.1.3. Determination of the flocculation capacity of chemical additives, "Flocculation volume (V, ml)" - p.29.

The results of the investigation and optimization of retention and drainage processes to improve the properties of paper suspensions and the clarity of the waters are scientifically applied and would serve researchers and paper producers to make the right and quick choice of type and amount of retention additive. The research provides new guidelines for the right combinations of types of fiber materials, type and amount of chemical additives and describes the expected results of their effectiveness.

When studying the drainage capacity of paper suspensions of secondary fibrous material from waste newsprint by six polyelectrolytes with different chemical nature and charge, it was

found that to improve the drainage and clarification of white waters, it is most appropriate to use chemical additives based on polyacrylamide at 0.025 ÷ 0.05% consumption.

3. Investigations for optimizing the multifunctional properties of different types of packaging materials.

3.1. Investigation and optimization of the properties of packaging materials with the addition of biopolymers - chitosan and rice starch.

In order to establish the effect of chitosan and a blends of chitosan and rice starch on the complex properties of printing papers and packaging materials, a series of experiments have been conducted for its use in paper both in suspension and at surface application and for film production [4_8; 7_10; 4_9; 4_10; 7_6].

The first stage of the experiment is to determine the effect of chitosan and a blends of chitosan and rice starch (5% and 7.5%) on viscoelastic, structural-dimensional, capillary-hygroscopic, barrier, physico-mechanical, optical, antibacterial properties and stability during thermal aging of the obtained paper samples [4_8; 7_10; 4_9]. In this study, additives were added in suspension to a fiber material of bleached sulphate softwood and hardwood pulp from spruce, pine and beech wood, and a modified cationic poly acrylamide was used as a retention additive.

When analyzing the dynamic mechanical properties of paper from cellulose, it was found out that there are two relaxation transitions, which suggests an inhomogeneous structure (cellulose consists of 50% mixture of pine and spruce and 50% beech). The first relaxation transition is less dominant and takes place in the temperature range 20–80 °C, while the second transition is more intense at 110-220 °C. During transitions, the supplied heat causes relaxation mobility, displacement and slippage of structural segments which spontaneously shrink. The temperature of the first relaxation transition, T_r , was 45.39 °C, and the second was 163.0 °C (determined from the slope of the curve of the storage modulus, E'). Since the relaxation transition of the pulp was more dominant in the second temperature range with greater damping and higher $\tan \delta$, we suggest that the main relaxation transition of the pulp can be assigned at 163 °C. Due to the supplied heat, the paper sample spontaneously shrank, since intermolecular and adhesive bonds between the structural elements were interrupted.

With the addition of retention aid, the relaxation transition regions of the paper have shifted. Two relaxation transitions still remain, but the main relaxation occurs in the first relaxation region, which is also shifted to lower temperature (between 0 °C and 50 °C). The lowering of the transition temperature is probably the consequence of the formation of free volume in the cellulose structure. The inclusion of branched retention polymers can increase the distance between parallel adjacent chains of cellulose, microfibrils, and cellulosic fibres and act as a plasticizer. During heating, newly formed looser structure gains a higher degree of kinetic freedom and mobility, so displacement and slippage of structural segments can occur at lower temperature (with a relaxation point at 15.83 °C).

Different relaxation transition temperatures are described for chitosan, ranging from 140 °C to 230 °C, while these reported values only apply for dry chitosan, but in the presence of moisture, the relaxation temperatures of chitosan are significantly reduced, as low as 30 °C for samples with water content ranging from 8 to 30 %. This is the consequence of the hygroscopic nature of chitosan, which is capable of forming hydrogen bonds with water molecules at ambient conditions (25 °C, 60% RH) through its amine and hydroxyl groups. Water-based hydrogen bonds can break

the intermolecular bonds of chitosan chains and cause a molecular rearrangement which eases the mobility of the structure and lowers the glass transition temperature of chitosan.

When mixed with pulp and retention aid, chitosan shows no relaxation transition in the temperature region where its transition point was found. In contrast, paper with chitosan (regardless of its concentration), similar to paper with retention aid, shows two temperature relaxation areas with increased transition temperatures.

Our results also show that the reduced stiffness of the paper with chitosan is not proportional to the amount of chitosan. The stiffness of the paper improved with 7.5% chitosan, but still remains lower than that for the paper with retention aid. With a higher amount of chitosan, there is more chance for water molecules to be fully bonded with chitosan molecules. When all molecules of water are bound, the unsaturated chitosan can bond with cellulose and the stiffness of the structure starts to rise again. With a higher amount of chitosan, there are more chances for chitosan to bond with cellulose and not with water. In both cases, more crosslinked structure is formed, which results in a higher relaxation transition temperature, as mentioned earlier. The formation of a more complex structure with higher amounts of added chitosan can also be confirmed by the curves of $\tan \delta$ and the mechanical loss modulus. In the case of a sample with a higher amount of chitosan, the temperature of the highest damping and scattering of heat is reduced, reflecting less intense friction of the structure due to its larger elastic response.

The viscoelastic curves of the rice starch sample show two relaxation areas at various temperatures: the first one, ranging from 15 to 45 °C with a transition point at 28.18 °C and the second, dominant one, consisting of many consecutive transitions, ranging from 45 to 95 °C with a transition point at 78.38 °C.

From the point of view of paper elasticity, dynamic mechanical analysis confirmed that addition of retention aid increased the elastic stiffness of the paper, so it is reasonably used for reinforcement of the paper structure. Adding chitosan alone or in combination with rice starch reduced the elasticity of paper. If 5% of chitosan content in paper is sufficient for papermaking needs, then it could be used in combination with low cost rice starch, since the elasticity of the paper does not decrease as much as at higher concentrations of chitosan. However, if larger amounts of chitosan (7.5 %) are used, its combination with rice starch is not appropriate, due to the resultant decrease in paper elasticity.

Despite the higher cost of chitosan, our research recommends the use of chitosan as an individual additive, since the results indicate a slight improvement in paper elasticity by raising the amount of chitosan in the fibres. Retention aid increases the elasticity and significantly reduces the relaxation transition temperature of the paper. Chitosan and rice are compatible with cellulose and therefore suitable for production of cellulose composites, but with some limitations, as stated below. Chitosan increases the relaxation transition temperature and reduces the elasticity of paper with retention aid. A mixture of chitosan and rice starch has little influence on the relaxation transition temperature but decreases paper elasticity.

The results of the studied grease resistance, hydrophobicity, strength and structure of the paper surface prove the positive effect of chitosan and a mixture of chitosan and rice starch. The addition of chitosan and rice starch reduces the pore size and increases the hydrophobicity of the papers. The binding of the cellulose matrix is altered by the presence of chitosan and rice starch, as well as the absorption of water. For paper, where 7.5 % of chitosan and rice starch were used, the water absorptiveness decreased by 33 %, compared to paper with only pulp. Grease resistance

of papers with fillers improved up to 88 %. Furthermore, smoothness and air permeability improved for papers with chitosan and rice starch. Chitosan and rice starch blends provided water and grease resistance, but not antibacterial activity against *Escherichia coli* K12. Therefore, preparing paper using a combination of chitosan and rice starch blend fillers is an improved and convenient procedure to enhance many properties of such papers. The study on the optical properties of the obtained samples of paper during accelerated thermal aging showed that the changes in color parameters during the studied 72 hours are similar and chitosan does not change significantly the ongoing aging processes, with largest positive effect at consumption of 7.5%.

The second part of the research [4_10; 7_6], aimed at determining the possibility of replacing synthetic-based packaging materials with "green", durable materials, which also have improved mechanical, antimicrobial and barrier properties. One of the most non-toxic and widely used polymers are polysaccharides, one of which is chitosan. Laboratory experiments were performed to obtain and characterize chitosan and rice starch films. For the purpose of the research, chitosan-rice starch films were obtained using ultrasonic treatment to improve the mechanical and optical properties.

The results showed that an ultrasonic treatment improved elasticity, moisture resistance and that films were more transparent. Elongation at break and tensile strength increased, especially at blend films. Moreover, moisture content showed a decrease proportional to an increase in thickness with decreasing film solubility at all treated samples. The surface at untreated blend film was more uneven compared to chitosan and rice starch films, which improved after the treatment. The ultrasonic treatment caused homogeneity of the surface and it is a good indicator for better structural and mechanical properties, compared to the untreated films. The surface of films improved at all treated films. The mechanical resistance of treated films was improved, especially at blend film. The results demonstrated that tensile strength increased with the ultrasonic treatment at all treated films. Better results of tensile strength are at treated samples and the maximum occurred at the blend of chitosan-rice starch film. The presence of rice starch in blend films can form highly cross-linked systems, preventing water molecules from penetrating into composite films. Such behaviour was confirmed at our research due to the inclusion of glycerol and rice starch as well, since they interfere with cross-links, resulting in decreased water solubility. In general, the ultrasonic treatment helps to obtain a smoother and homogeneous surface. New studies are necessary to find the best ultrasonic procedures (regarding treatment times and frequency) to prepare the films.

The conducted experiments for optimizing the properties of packaging materials with the addition of biopolymers - chitosan and rice starch have a significant scientific contribution to the analysis of the dynamic mechanical properties of paper from bleached softwood and hardwood pulp from spruce, pine and beech wood. Due to the complex anisotropic nature of the paper, research in the field of viscoelastic properties of paper is extremely rare.

The two relaxation transitions found in the experiments confirm the inhomogeneous structure of the paper. The defined exact zones and temperatures of the relaxation transitions of the used pulps and papers characterize with great accuracy the influence of the type and consumption of each additive used in the paper (retention, chitosan and starch) and contribute to increasing knowledge about the viscoelastic properties of paper.

3.2. Investigation and optimization on the antibacterial properties of packaging materials with the addition of plant extracts, silver nanoparticles and others.

Research and development of new plant fiber-based packaging materials for active and intelligent packaging shows huge potential to optimize the supply chain and to extend the shelf life of food products and to increase consumer awareness of food utilization. After studies on the existing solutions in the scientific literature and the trade network [8_16; 8_17; 8_21; 8_5] it was found out that a relatively new and promising way to achieve this goal is to obtain packaging papers with antibacterial properties, using plant extracts of various Bulgarian herbs.

In the conducted research [8_4; 8_27; 8_29], liquid extracts of plants essential oil were obtained: thyme (*Thymus vulgaris* L.), basil (*Ocimum basilicum* L.), rosemary (*Rosmarinus officinalis* L.), St. John's-wort (*Hypericum perforatum* L.), caraway fruits (*Carum carvi* L.). Three types of paper were used in the experiments: from bleached pulp, 100% recycled paper and unbleached pulp for packaging application.

To determine the antimicrobial effect of the extracts of cumin, basil, thyme, rosemary and St. John's-wort were used test cultures - from the National Bank for Industrial Microorganisms and Cell Cultures, Sofia - Gram-positive: *Staphylococcus aureus* ATCC 6538; *Bacillus subtilis* ATCC 6633; *Kocuria rhizophila* ATCC 9341 and Gram-negative: *Escherichia coli* ATCC 8739; *Pseudomonas aeruginosa* ATCC 9027; *Salmonella abony* NTCC 6017. Yeast was also used: *Saccharomyces cerevisiae* ATCC 9763; *Candida albicans* ATCC 10231, as well as fungi: *Aspergillus brasiliensis* ATCC 16404; *Fusarium moniliformae*. The samples were cultured in a thermostat at $35^{\circ}\text{C} \pm 2^{\circ}\text{C}$ for 24-48 hours.

Bleached cellulose paper treated with rosemary extract showed the largest reduction by 76.1% in the number of viable microorganisms in *Staphylococcus aureus*, by 72% in *Bacillus subtilis* and 84% in *Salmonella abony*. Treatment with other extracts has little or no effect, reducing the number of viable microorganisms by between 0 and 55%.

Treatment of recycled paper with rosemary extract caused a reduction in the number of viable cells by 74% in *Staphylococcus aureus*, by 78.5% in *Bacillus subtilis* and by 70.3% in *Salmonella abony*. Caraway, thyme and St. John's-wort extracts caused a reduction in the number of viable cells in *Bacillus subtilis* by 52.5%, 50% and 67.5%, respectively.

Treatment of unbleached cellulose wrapping paper with rosemary extract reduced the number of viable cells by 80% in *Staphylococcus aureus*, by 66% in *Bacillus subtilis* and by 20% in *Salmonella abony*.

The results show that treatment with rosemary extract has the strongest effect on all three types of paper. The physico-mechanical properties do not have a significant decrease and are practically unchanged. This gives basis for the plant extracts of rosemary, cumin basil and thyme to be recommended for processing different types of paper and making active packaging.

In another study [4_6] the possibilities of using silver nanoparticles in the composition of packaging papers were considered. In the laboratory conditions, silver nanoparticles were obtained with the help of ultrasound, microbiological studies of paper samples were performed and physico-mechanical properties of the commissioned papers were studied.

Due to its low cost and easy implementation, both in laboratory and industrial conditions, the method for synthesis of silver nanoparticles using an ultrasonic field is an interesting alternative compared to other known methods. A comprehensive study is conducted on the influence of

parameters, which were used to obtain suspensions that contain silver particles. Their presence was proved by atomic absorption analysis. Fluorescence microscopy studies have shown the existence of a very small amount of aggregated particles up to several microns in size. We successfully integrated the obtained suspensions into the pulp in order to obtain paper samples, which were tested for antibacterial activity. The results of this study show that Gram-negative *Escherichia coli* bacteria cannot pass through cellulosic surfaces containing silver particles. There was a decrease in the value of elongation at break in the range of 2-3%. This shows that silver nanoparticles practically do not change the physical and mechanical characteristics, but the paper acts as a barrier to bacteria and could be used as a packaging material for food.

Other methods for imparting antibacterial properties to packaging materials is to investigate the possibility of wood preservation by modification with various substances (alkaline-activated hydrolysis lignin, Cu₂S and maleic anhydride) by the method of impregnation through hot and cold baths [7_5] and to study the impact of the process on some operational properties of the wood material.

The experiments were conducted with poplar wood (samples 10x1x1 cm), which has low density with well-developed capillary system, good absorption capacity and belongs to low operational capacities tree species. Alkaline activated hydrolysis lignin (AAHL), Cu₂S and Maleic anhydride (MA) were used to modify the poplar wood. The modification was carried out by the hot and cold bathing method. The modified samples were characterized by Fourier-transform infrared spectroscopy (FTIR), differential thermogravimetry (DTG) and thermogravimetric analysis (TG), water absorption and antibacterial activity against *Bacillus subtilis* (G+) and *Escherichia coli* K12 (G-).

The IR spectra of the modified samples showed changes in the structure of wood samples as a result of physical and chemical processes. DTG and TG methods were used to monitor the change in samples weight as a function of temperature.

By comparing the weight loss of the three types of modified wood samples it was found out that the used AAHL and Cu₂S substances have a positive influence on the thermal stability, having retardant effect.

The obtained results showed that samples modified with maleic anhydride and Cu₂S have reduced water absorption. The investigated modified wood samples exhibit antibacterial activity against *Escherichia coli* K12. Best antibacterial effect was observed by sample modified with maleic anhydride.

The conducted experiments for characterization and optimization of the antibacterial properties of packaging materials by adding plant extracts, silver nanoparticles, copper sulfate, maleic anhydride, etc. are of significant scientific and applied nature.

The characterized antibacterial properties of the obtained papers, treated with extracts of five species of essential oil plants and silver nanoparticles, with respect to ten microorganisms and cell cultures, claim to be circumstantiality. The research data are useful for refining the type of microorganisms and cell cultures for laboratory experiments. The derived conclusions allow optimal selection of type and application of antimicrobial agent for active wrapping papers, cardboards, wood composites, etc.

4. Investigation on the properties of corrugated cardboard for optimizing the processes of its obtaining and processing.

Paper industry and humanity are connected in many different ways. Every moment we rely on a product made of paper and cardboard. More than 1200 different types of products are made specifically from paper or with its participation. More than 70% of cardboard in the world is used for the production of packaging, 10-15% - for construction purposes, and the remaining amount is distributed between technical and special types of cardboard for various purposes.

The main materials used for the production of corrugated cardboard are the papers for the corrugated layer and the papers and cardboards for the liner layers. The indicators of these papers and cardboards largely determine the quality of corrugated cardboard [8_14; 8_20; 8_21]. A number of specific properties of corrugated cardboard and its packaging are related to the quality or more precisely to the properties and performance of its liner layers - resistance to cracking, crushing at the edge, appearance, printability, etc., and others are determined mainly from the quality and properties of the corrugated paper - resistance to flat crushing, amortization ability, hardness, etc. In addition to high mechanical strength, the outer liner layer must have sufficient smoothness and strength of the surface. Without complying with this requirement, it is difficult to produce the corrugated cardboard of modern technological lines and especially the application of printing.

Trends in the production of corrugated cardboard are for increasing the use of test liners with both white top and classic, instead of kraft liners. The general tendency to reduce the basic weight of the paper is also valid for corrugated board papers.

A study [8_14] is conducted with twelve types of test liner papers, three types of kraft liner papers and six fluting papers used for the production of corrugated cardboard, provided by Dunapack Rodina - Plovdiv. Microscopic analysis was performed on all examined papers to determine the fiber composition and the structural-dimensional, capillary-hygroscopic, physico-mechanical and deformation properties were determined.

In terms of capillary-hygroscopic properties (Cobb₆₀ water absorption), white top test liners have the highest degree of sizing, followed by classic (brown) test liners and craft liners. According to their strength indicators, the studied liners are arranged in the following descending order: Kraft liner – Test liner with white top layer – Test liner - Schrenz, and according to their importance for the strength of the finished package of dynamic loads, physical-mechanical and deformation properties are arranged in the following descending order: Tearing - Hardness - Bursting - Tensile – Bending resistance.

When designing different products, it is often necessary to perform some calculations in terms of strength indicators, which will allow for its more efficient use. There are a number of analytically and experimentally derived dependencies, which make it possible to determine some indicators that give a more realistic idea of the behavior of corrugated cardboard under real conditions.

It is impossible to create models that fully describe the features of corrugated cardboard packaging. A need to respond more fully to reality leads to their excessive complication, which in most cases does not give the expected results. In order to obtain closer to reality results in the study of these models, it is necessary to know the behavior of the material at different loads.

The purpose of the research [8_20; 8_21] is to collect and present data on the resistance of corrugated board materials to edge crush (ECT) and flat crushing resistance (FCT) on untreated and treated corrugated board and to compare them with the theoretically calculated values of these two indicators depending on the composition of the material, in order to achieve predictability of the strength and deformation properties of corrugated cardboard and its packaging, to optimize the production process and save materials and resources.

For the needs of the research, samples of six types of three-layered and four types of five-layered corrugated cardboard were tested. The two studied indicators make it possible to theoretically determine the indicator BCT - Box Compression Test according to the formula of McKee and to compare with the experimentally obtained ones.

It has been found out that the ECT indicator depends on two main factors: the type of the flute and the basic weight of the paper used to produce corrugated board. The first factor is related to the flat crushing resistance FCT, which correlates with $CMT - FCT = 0,11 \cdot CMT + 0,24$.

In the case of double face corrugated board, the difference between the theoretically determined ECT and the experimentally obtained ECT after processing depends on the flute size and the type of paper used. The smaller the flute, the smaller the difference in the indicator and it is in the range of 1.5-2 kN/m. The double face corrugated board, produced with a corrugated layer, of paper with reinforced properties, gives smaller differences for the ECT indicator, theoretically calculated and experimentally determined. The difference between the experimentally determined ECT of the double face corrugated cardboard before and after processing is in the range of 0.2-0.5 kN/m and depends on what type of machine the cardboard is processed - flat or slotted machine. In the case of flat, the difference is smaller. In the case of the FCT indicator, the difference between the theoretical calculations and the experimentally determined after processing indicator is 35-70 kPa, with a greater influence on the basic weight of the paper and not on the type of the flute.

In the case of triple face corrugated board, the difference between the theoretically determined ECT and the experimentally obtained ECT after processing depends on the flute size and the type of paper used and is in the range of 2.4-3 kN/m. The triple face corrugated board, produced with a corrugated layer of paper with reinforced properties, gives smaller differences for the ECT indicator, theoretically calculated and experimentally determined. The difference between the experimentally determined ECT of the triple face corrugated cardboard before and after processing is in the range of 1.3-2.0 kN/m and depends on what type of machine the cardboard is processed - flat punch or slotted machine. In the case of flat, the difference is smaller.

The investigations on the properties of the most used in practice types of double and triple face corrugated cardboards, characterizing their operational qualities, have first of all a scientific-applied character. Based on the obtained new data for exact values for the difference between the theoretically calculated and experimentally determined deformation indicators of corrugated cardboard, all manufacturers could optimize the processes without a loss of materials and time. The results help to predict the pressure resistance of the finished corrugated cardboard packaging during palletizing and transport.

5. Others.

Computer Aided Design (CAD) includes the full range of computer generated packaging modeling techniques, from modeling to creating an animation according to users' requirements. CAD systems are software for the development of engineering and architectural projects with the possibility of two-dimensional (2D) and three-dimensional (3D) model representation.

Designers' work, as a stage of the production process, always begins with the design of the package. The main dimensions, the material for making the package (type of cardboard, thickness, presence of coating, type of face layer, etc.) are specified, the structure of the body, the small and large lids of the package is developed, the places for folding and gluing, determine whether and where the coating and Braille text will be applied.

The main activity of the designers is to adapt an existing designs or to create variants of existing products to new requirements. The original designs are only a small part. In case the design task is an adaptive or variant construction, the already known principles of the solution are preserved, but the components are modified according to the new requirements. This type of design often involves routine activities, as the basic structure of the components remains unchanged, but knowledge of trends [8_13], the basic elements of the structure [8_15], the relationships between them and the parameters and properties of the material from which they will be made are essential for a successful and fast process of creating an optimal product in terms of: structure - material - quality - workflow [8_25].

Following the main processes from design and production of display and packaging for souvenirs to the stage of their approved real sample before production, specialized software for packaging design EngView Package and Display Designer is used [8_25]. It was found that the process from the idea to inception of the packaging is a workflow that should be conformable to the materials, technology, market and consumer needs and even more.

The contemporary design of the packaging and their appropriate commercial realization involves the usage of a large number of software products that repeatedly shortened steps in the design but requires a specific knowledge of the exact materials of which the packaging should be produced and specific technologies that enable the successful implementation of the original idea.

The contributions are of applied-methodical character for training of the students and their knowledge skills for real applications in production conditions.