THE MINISTRY OF HIGHER AND SECONDARY
SPECIAL EDUCATION
OF THE REPUBLIC OF UZBEKISTAN
MASTERS DEPARTMENT OF BUKHARA STATE UNIVERSITY
BUKHARA STATE UNIVERSITY
FACULTY OF NATURAL SCIENCES
DEPARTMENT OF CHEMISTRY

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CREATION OF NANOCOMPOSITES FOR THE TEXTILE INDUSTRY BASED ON MODIFIED STARCH AND LOCAL POLYMERS.

5A140501-chemistry

Graduation thesis on competition
academic degree of master

Scientific supervisor: **candidate of chemical Sciences,**
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BUKHARA - 2018

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ЎЗБЕКИСТОН РЕСПУБЛИКАСИ ОЛИЙ ВА ЎРТА МАХСУС ТАЪЛИМ ВАЗИРЛИГИ

БУХОРО ДАВЛАТ УНИВЕРСИТЕТИ

Факультет: ***Табиий фанлар***
Магистратура талабаси: **Олимов Бобир Баҳодир ўғли**

Кафедра: ***Кимё***
Илмий раҳбар: **Равшанов Қазоқмурод Асадович**

Ўқув йили: ***2016-2018***
Таълим йуналиши: **5 А140501- Кимё (Ноорганик кимё) мутахасислиги**

МАГИСТРЛИК ДИССЕРТАЦИЯ АННОТАЦИЯСИ

Мавзунинг долзарблиги. Бозор муносабатларида юқори сифатли ва рақобатбардош маҳсулотларни ишлаб чиқариш ҳозирги замоннинг талаби ва тўқимачилик саноатининг бирдан бир омили ҳисобланади. Ҳозирги вақтда тўқимачилик саноатида пахта толасини қайта ишлаш, мамлакатимизда илмий-техникавий асосни ҳамда юқори сифатли тўқимачилик саноат маҳсулотларининг физик-кимёвий ва физик-механик хоссаларини ўрганишни талаб қилади. Қуюқлаштирувчилар тўқимачилик саноат маҳсулотларини ишлаб чиқаришда асосий ролни ўйнайди, уни ишлаб чиқарувчилар иқтисодий жиҳатдан нархининг арзонлиги ва сифатининг юқорилигини таъминлаши, унинг технологик хоссасини яхшилаш, бўёвчи моддаларнинг фойдаланиш даражасини оширишини таъминлаши керак. Кўпгина тўқимачилик саноат пардозлаш корхоналарида матоларга фаол бўёқлар билан гул босишда табиий крахмал қўлланилмайди, унинг ўрнига хориждан келтирилаётган қуюқлаштирувчилар ишлатилади. Бу эса маҳсулот таннархининг ошишига, етказиб бериш муддатининг жудаям чўзилиб кетишига ва мамлакатнинг валюта захирасига катта таъсир кўрсатади. Ҳеч қайси бир полимерни индивидуал қуюқлаштирувчи сифатида ишлатиб бўлмаганлиги сабабли нанокомпозицион полимерлар асосида қуюқлаштирувчилардан фойдаланиш муҳим аҳамият касб этмоқда.

Пахта толаси асосидаги тўқимачилик матоларига гул босиш жараёни учун республикамизда ишлаб чиқариладиган табиий полимер ва кимёвий реагентлар асосида яхши натижа берувчи таркибли ва тузилишли нанокомпозит куюқлаштирувчилар яратиш долзарб муаммолардан бири ҳисобланади. Бундай кўп функцияли полимер материалларни ишлаб чиқиш сувда эрувчан полимер фосфатли тузлар асосида крахмал фосфат ишлаб чиқариладиган, хамда маҳаллий саноат корхоналарида ишлаб чиқариладиган синтетик полимерлардан нанокомпозицион қуюқлаштирувчилар таркибини яратишдан иборат.

Мавзунинг мақсади: Маҳаллий хом ашёлар асосида олинган модификацияланган крахмал (МК) ва сувда эрувчан полимерлар унифлок, гидролизланган полиакрилонитрил (ГИПАН) ҳамда полиакриламид (ПАА) асосида нанокомпозицион қуюқлаштирувчи маҳсулотлар олиш ва унинг физик-кимёвий хоссаларини ўрганиш.

Мавзунинг вазифалари: Иш мақсадидан келиб чиққан ҳолда қуйидаги вазифалар белгиланди.

1. Матога фаол бўёқларни босиш учун модификацияланган крахмал ва сувда эрувчан полимерлар асосида қуюқлаштирувчиларнинг таркибини ишлаб чиқиш;
2. Нанокомпозицион қуюқлаштирувчиларнинг тузилиш, реологик ва матоларга гул босиш технологиясини ўрганиш;
3. Ишлаб чиқилган нанокомпозицион қуюқлаштирувчиларнинг матога гул босишдаги физик-механик ва колористик хусусиятларини ўрганиш.

Тадқиқот объекти ва предмети. Модификацияланган крахмал (МК), синтетик полимерлар – унифлок, гидролизланган полиакрилонитрил (ГИПАН) ҳамда полиакриламид (ПАА).

Тадқиқот усуллари. Вискозиметрия, кимёвий анализ, визуал ва спектрал тадкикот усуллари.

Тадқиқот методлари. Крахмал ва синтетик полимерларнинг таркиби, физик-кимёвий хоссалари ва тузилиши ўрганилади, модификацияланган крахмал (МК) ва сувда эрувчан полимерлар унифлок, гидролизланган полиакрилонитрил (ГИПАН) ҳамда полиакриламид (ПАА) лардан олинган нанокомпозит материалларнинг реологик хоссалари тадқиқ этилади

Тадқиқот натижаларининг илмий жиҳатдан янгилик даражаси:

Маҳаллий хом ашёлар асосида олинган модификацияланган крахмал (МК) ва сувда эрувчан полимерлар унифлок, гидролизланган полиакрилонитрил (ГИПАН) ҳамда полиакриламид (ПАА) асосида қуюқлаштирувчи нанокомпозициялар олишнинг илмий асосини яратиш. Қуюқлаштирувчи нанокомпозициялар таркибига кирувчи компонентлар ва уларнинг функционал гуруҳлар таркибий қисмларининг бир-бирига мойиллигини ўрганиш. Қуюқлаштирувчи нанокомпозициялар олиш жараёнида таркиб ва тузилиш ўзгаришини физик-кимёвий асослаб, маҳаллий хом ашёларга асосланган ҳолда қуюқлаштирувчи нанокомпозициялар олишнинг энг мақбул ва ресурс тежамкор технологиясини ишлаб чиқиш

Тадқиқот натижаларининг амалий аҳамияти: Ишлаб чиқилган қуюқлаштирувчи хусусиятга эга бўлган нанокомпозицияларни ишлаб чиқаришнинг пардозлаш цехларида қўллаш ва уни самарадорлигини аниқлаш.

Иш тузилиши ва таркиби Кириш қисмида мавзунинг долзарблиги асослаб берилади, ўтказилган тадқиқотларнинг мақсад ва вазифалари шакллантирилиб, ишнинг илмий янгилиги ва амалий аҳамияти кўрсатилади.

Биринчи бобда мамлакатимиз ва чет эл тўқимачилик саноатида қўлланиладиган қуюқлаштирувчиларнинг ҳозирги кундаги ҳолати ва ривожланиш тенденцияси ҳақидаги илмий – техник ишларнинг таҳлили берилади.

Иккинчи бобда тадқиқот усуллари тавсифланди ва қўлланилган материаллар ҳақида маълумотлар келтирилади.

Учинчи бобда илмий техник адабиётлар таҳлили натижасида шакллантирилган, маҳаллий хом-ашёларга асосланган қуюқлаштирувчи нанокомпозитлар таркиби ишлаб чиқилади, уларнинг физик-кимёвий, механик ва реологик хоссалари ўрганилади, ишлаб-чиқилган таркибнинг қуюқлаштирувчи полимер нанокомпозиция хусусиятлари ишлаб-чиқариш синовидан ўтказиш режалаштирилади.

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БУХАРСКИЙ ГОСУДАРСТВЕННЫЙ УНИВЕРСИТЕТ

ФАКУЛЬТЕТ ЕСТЕСТВЕННЫХ НАУК

КАФЕДРА ХИМИИ

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АННОТАЦИЯ

Актуальность темы. В современных условиях формирования рыночных отношений повышение качества и конкурентоспособности продукции является одной из ключевых задач в текстильной промышленности, решаемых путем создания эффективных безотходных технологий, позволяющих значительно снизить или полностью исключить применение дорогих импортных, привозных химических материалов. В настоящее время для печатания хлопчатобумажной ткани в текстильной промышленности, как и у нас в стране так и за рубежом разрабатываются научно-технические решения, предусматривающие получение высокоэффективных текстильных материалов с заданными физико-химическими и физико-механическими свойствами.

Загущающие материалы играют вспомогательную роль в текстильном производстве, тем не менее, их стоимость и качество ощутимо влияют на экономические показатели отделочного производства, а улучшение ее технологических свойств создает предпосылки для удешевления печати за счет повышения степени полезного использования красителя. Во многих текстильных предприятиях с активными красителями уже не используется нативной крахмал, причем применяется дорогие импортные загустители, которые ощутимо влияет на цену продукта и обусловливает связанность производств, с их доставкой расходуя не только много времени, но и валютных резерв государства.

Поскольку ни один индивидуальный полимер не может использоваться в качестве совершенного загустителя, создание легконаносимых (технологичных) покрытий для текстильных материалов возможно на основе полимерных композиций. Поэтому весьма актуальной задачей является разработка состава и рецептуры эффективных композиций на основе местного полимерного сырья как природного так и синтетических происхождений, пригодного в качестве загустки в процессе отделки хлопчатобумажных тканей. В этом аспекте несомненный интерес представляют полифункциональные полимерные композиции на основе водорастворимого полимера, унифлок (УФК) и гидролизованный полиакрилонитрил (ГИПАН) производимая в АОО «Навоиазот», а также окисленно модифицированный крахмал (ОМК), полученный из рисовой муки, которым является вторичным продуктом при переработке риса.

Соответствие работы приоритетным направлением научных исследований в республике, степень изученности проблемы, связь работы с планами научно-исследовательских работ.

Данная работа выполняется в рамках исследований проводимых в научном лаборатории кафедры «Химии» Бухарского государственного университета по теме «Разработка технологии получения полимеров на основе гетероциклических соединений и исследование их промышленно–технологических свойств» (номер гос. регистрации 0197000630), координируемой научным советом «Новые вещества, процессы получения и переработки» АН РУз, а также составной частью государственного фундаментального научно - исследовательского проекта государственного гранта Республики Узбекистан по проекту ЁА-12-8 на тему «Модификация крахмала и создание технологии получения новых импортозамещающих загущающих материалов на его основе» выполняемый в 2016-2017 годах.

Целью настоящей работы является разработка технологии получения новых составов высокоэффективных композиционных загустителей на основе ОМК, синтезированного из рисового крахмала полученного из вторичного сырья при переработки сельскохозяйственных культур и водорастворимых полимеров применяемые в процессе печатания хлопчатобумажной ткани в качестве загустителя печатной краски. Разработка направлена на интенсификации процесса печатания, расширению сырьевой базы, упрощению технологи производства и снижение себестоимости выпускаемых продукций.

Объектами исследований работы являются окисленный крахмал, полимеры гидролизованного полиакрилонитрила и препарата унифлок.

Предмет исследований дипломной работы снижение энерго- и ресурсоемкости отделочного производства путем получения высокоэффективных загустителей, обеспечивающий хорошие качества рисунков на тканях, разработка физико-химических и технологических основ получения загусток, путем комбинированной модификации крахмала путем окисления и присутствии водорастворимых полимеров, а также набивка хлопчатобумажных тканей с активными красителями на основе помощью разработанных загусток в лабораторных условиях текстильной производстве.

Новизна результатов, ожидаемых от выполнения выпускной работы. Будут созданы новые загустители на основе окисленного крахмала и водорастворимых полимеров. Составы разрабатываемых полимерных композиций пригодных в качестве загустителей для набивки хлопчатобумажной ткани, позволяют улучшить технологические и физико-механические свойства набивных тканей. Предполагается, что за счет модификации крахмала путем окисленной модификации, а также применение синтетических полимеров, возможно, получается достаточно пластические массы загустителя с необходимой вязкостью. Будут разработаны оптимальные составы загустителей и печатных красок с активными и диазо- красителями.

Сведения о планируемых работах и методах исследований. При выполнении работы будут решены следующие научно-технические задачи:

- разработка состава загустителей на основе модифицированного крахмала и водорастворимых полимеров для набивки тканей с активными и диазокрасителями;
- изучение структурно-механических, реологических и печатно-технических свойств композиций;
- изучение физико-механических, технических и колористических свойств набивных тканей печатанных разработанными композициями;

Научные исследования по работе будут проведены с применением традиционных загустителей для приготовления печатных красок и основываясь на новых композиционных загущающих материалов. Особенности приготовления заглушающих композиций на ее основе будут изучены с применением комплекса химических, механических, оптических и электронно-микроскопических методов исследования.

Объем и структура работы. Работа изложена на 60 страницах, содержит рисунков и таблицы и состоит из введения, трех глав, основных выводов, списка литературы из 92 наименований и приложения.

В первой главе представлены анализ научно-технических работ касающихся изучении состава и структуре крахмала разных плодов и его модификаций, непосредственно связанных с темой данного исследования. Особое внимание уделено применению композиционных материалов, на основе модифицированного крахмала, используемых для печатания текстильных материалов. В заключительном разделе литературного обзора сформулированы цели и задачи работы.

Во второй главе описаны методы исследования, применяемые в работе: методика создание композиций на основе модифицированного крахмала с гидрозованном полиакрилонитрилом и унифлоком, получения плёнки, определения вязкости композиций, и исследований других свойств полученных композиций.

Третья глава посвящена обсуждению результатов созданы и изучению композиций на основе модифицированного крахмала, который применяются в качестве загустки и изучении структурно-механических и реологических свойств композиции загусток. Сформулирован критерий оценки печатания хлопчатобумажной ткани, загущающими композициями в лабораторных условиях. Составлены уравнение регрессии описывающие зависимость реологических свойств композиции, а также колористические свойства напечатанных тканей.

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ANNOTATION

Relevance of the topic. In the current conditions of the formation of market relations, improving the quality and competitiveness of products is one of the key tasks in the textile industry, which are solved by creating effective non-waste technologies that allow to significantly reduce or completely eliminate the use of expensive import, imported chemical materials. At the present time, for the printing of cotton fabric in the textile industry, as in our country and abroad, scientific and technical solutions are being developed that provide for the production of highly effective textile materials with prescribed physical-chemical and physical-mechanical properties.

Thickening materials play an auxiliary role in textile production, however, their cost and quality significantly affect the economic performance of finishing production, and improving its technological properties creates the prerequisites for reducing the cost of printing by increasing the degree of useful use of the dye. Many textile enterprises with active dyes no longer use native starch, and expensive imported thickeners are used, which significantly affects the price of the product and causes the connectedness of production, with their delivery spending not only a lot of time, but also the foreign exchange reserves of the state.

Since no single polymer can be used as a perfect thickener, it is possible to create light-weight (technological) coatings for textile materials on the basis of polymer compositions. Therefore, a very urgent task is to develop the composition

and formulation of effective compositions based on local polymeric raw materials of both natural and synthetic origin, suitable as a thickener in the process of finishing cotton fabrics. In this aspect, polyfunctional polymer compositions based on the water-soluble polymer, unifloc (UFC) produced in the "Navoiazot" LLC, microcrystalline cellulose (MCC) produced in JSC "Ferganaazot", and finally the electrochemical modified starch (EMC) obtained from rice flour, which is a secondary product when processing rice.

The correspondence of work with the priority direction of scientific research in the republic, the degree of study of the problem, the connection of work with plans for research work.

This work is carried out in the framework of research conducted in the scientific laboratory of the Department of "Chemistry" of the Bukhara State University on the topic "Development of technology for the preparation of polymers based on heterocyclic compounds and the study of their industrial and technological properties" (state registration number 0197000630) coordinated by the Scientific Council "New substances , the processes of obtaining and processing »of the Academy of Sciences of Uzbekistan, as well as an integral part of the state fundamental research project of the state grant of the Republic of Uzbekistan on project EOA-12-8 on the theme "Modification of starch and creation of technology for obtaining new import-substituting thickening materials based on it" carried out in 2016-2017.

The purpose of this work is to develop a technology for the preparation of new compositions of highly effective composite thickeners based on EHM, synthesized from rice starch derived from recycled materials during processing of agricultural crops and water-soluble polymers used in the printing of cotton fabric as a thickener of printing ink. The development is aimed at intensifying the printing process, expanding the raw material base, simplifying production technologies and reducing the cost of manufactured products.

The objects of research work are electrochemical modified starch, microcrystalline cellulose and unifloc.

The subject of the research work is the reduction of energy and resource intensity of finishing production by obtaining highly effective thickeners, ensuring good quality of the drawings on the tissues, developing the physicochemical and technological basis for obtaining clots, by combining the modification of starch by oxidation and the presence of water-soluble polymers, and packing cotton fabrics with active dyes on the basis of developed clots in laboratory conditions of textile production.

Novelty of the results expected from the performance of the final work. New thickeners based on oxidized starch and water-soluble polymers will be created. Compositions of polymer compositions being developed suitable as thickeners for packing cotton fabric, allow improving the technological and physical-mechanical properties of printed fabrics. It is assumed that due to the modification of starch by electrochemical modification, as well as the use of synthetic polymers, it is possible to obtain sufficiently plastic masses of the thickener with the required viscosity. Optimum compositions of thickeners and printing inks with active and cold dyes will be developed.

Information about the planned works and methods of research. In carrying out the work, the following scientific and technical tasks will be solved:

- development of the composition of thickeners based on modified starch and water-soluble polymers for filling fabrics with active and cold dyes;
- study of structural-mechanical, rheological and printing-technical properties of compositions;
- study of physical-mechanical, technical and color characteristics of printed fabrics printed with developed compositions.

Scientific research on the work will be carried out using traditional thickeners for the preparation of printing inks and based on new composite thickening materials. The peculiarities of the process of starch modification and the preparation of fizzy compositions based on it will be studied using a complex of chemical, mechanical, optical and electron microscopic methods of investigation.

Scope and structure of work. The work is presented in 60 pages, contains drawings and tables and consists of an introduction, four chapters, main conclusions, a list of literature from the titles and applications.

The first chapter presents an analysis of scientific and technical works concerning the study of the composition and structure of starch of different fruits and its modifications directly related to the topic of this study. Particular attention is paid to the use of composite materials, based on modified starch, used for printing textile materials. The final section of the literary review sets out the goals and objectives of the work.

The second chapter describes the research methods used in the work: the technique of creating compositions based on modified starch with hydrated polyacrylonitrile and unifloc, obtaining a skin, determining the viscosity of the compositions, and examining other properties of the compositions obtained.

The third chapter is devoted to the discussion of the results of the creation and study of compositions based on modified starch, which is used as a thickener and to study the structural-mechanical and rheological properties of the composition of the thickener. The criterion for evaluating the printing of cotton fabric, thickening compositions in laboratory conditions is formulated. The regression equation describing the dependence of the rheological properties of the composition, as well as the coloristic properties of the printed tissues, is compiled.

CHAPTER I. Literary Review

1.1. Composition and structure of natural starches and modern methods their research.

Starch is a highly polymeric substance from the group of polysaccharides. Starch is the most common carbohydrate of plants, which is formed in leaves as a result of photosynthesis and deposited in roots, tubers and seeds in the form of grains. Grains have a size, shape and internal structure, characteristic for each plant species. For the size of starch grains take the length of their largest axis in microns. The average sizes of starch grains of various origins vary widely. The largest are the grains of potato - 17-35 microns, the smallest - starch grains of millet and rice 5-7 microns [1,2]. Researchers [3] note that small starch grains of cereal crops have a higher gelatinization temperature than large ones. This property is explained by the increased protein content in fine grains. It is suggested that the associated protein protects the grains from destruction, and also promotes the formation of aggregates with hemicellulose and glycons. Properties such as solubility, swelling, absorption and adsorption directly depend on the specific surface area of the starch particles [2]. The rate of water adsorption increases with decreasing starch particle size and depends on the initial water content in the starch [4].

Starchy grains are heterogeneous, in addition to polysaccharides, they contain water (10 + 20%) and in very small amounts (a total of 0.5-2%) cellulose, phosphates, silica, fatty acids, lipids and protein residues. And the researchers report a high dependence of the content of these components on agronomical measures [1,5]. It was noted that with the increase in the amount of fertilizers applied, the ash, phosphorus, potassium and magnesium content tend to decrease, and the calcium content to growth [2]. In general, the stable characteristics of starch gels are a sign of heredity associated with climate [6]. The content of cations bound by phosphates is determined by atomic absorption spectrometry [1, 7]. The results of analysis of different types of potato starch showed that the content of cations in 100 g of sample varies within the limits of: P 28-90; K 19-58; Mg 6-16 and Ca 0.9-3.6 mg. For more accurate determination of cation content, it is preferable to extract them from starch instead of ashing [7].

Polysaccharides of starch consist of the residues of D-glucose in its α-D-glycopyranose form and differ in the degree of polymerization and the nature of the bonds of α-D-glycopyranose units. Proceeding from this, polysaccharides can be divided into two main fractions: amylose and amylopectin.

Amylose molecules are linear or very slightly branched chains consisting of 200 + 1000 D-glucose residues, which are linked together by α-1,4-glucosidic bonds, at the branching sites, glucose residues in amylose form α-1,6 bonds. Amylose also contains a small amount of β-1,2-, 3-1,3- and 3-1,4-glucosidic bonds. According to the type of structure, amylose is similar to fiber, differing from the latter by the presence of α-bonds (in the cellulose glycopyranose residues form β-bonds) and the spatial configuration of macromolecules [8]. Using NMR13C spectroscopy and wide-angle X-ray diffraction [9, 10], the spiral structure of amylose macromolecules in aqueous solution was proved. One turn of the spiral consists, as a rule, of 6-8 glucose residues. High-molecular amylose forms an impaired, i.e. intermittent, or deformed helix. At these stressed points, the glycoside compounds can rotate so that the molecule twists. Thus, amylose, which consists of separate spiral segments, behaves like a statistical coil like many linear polymers. Due to the spiral conformation of the macromolecules, amylose forms stable crystalline complexes with alcohols, fatty acids, phenols, nitroparaffins and pyridine [11, 12].

The molecular weight of polysaccharides of the amylose fraction, determined by ultracentrifugation [13], is 200 ± 250 thousand for corn starch and 1,000 thousand for potato starch. Amylopectin macromolecules are highly branched, they contain from 600 to 6000 residues of D-glucose, linked together by α-1,4-glucosidic bonds, and at the branching sites α -1,6-bonds. In the amylopectin, a small number of 1,3-bonds was also found [8]. There are two types of side chains: L - chains, consisting of approximately 45 elementary units and 8 chains, consisting of 15-20 elementary units. An estimate of the ratio of the side chains showed [14] that the average value of this ratio is 1.69. The molecular weight of amylopectin reaches (50 + 500) x10

[13]. Side chains of amylopectin, separated by the enzymatic method [15] by mass fraction were 64% for potato starch and 62.7% for corn, the length of the cleaved side chains was 12 elementary units and the spacing between these chains of 7 elementary links.

It is assumed that the conformation of amylopectin macromolecules is intermediate between linear and globular, it is attributed to the compactness characteristic of a branched polymer [16].

The origin of the starch	Content	
	amylose, %	amylopectin, %
potato (24 sorts)	19-24	76-81
the sweet potato (22 kinds)	17,5-21,7	79-82
corn (39 sorts)	22,2-28,3	~73
rice (19 sorts)	12,9-25,5	~78
oats	25,0	~75
wheat	25-26	~74,5
barley	16,7	~83
tapioca	17	83

The ratio of amylose and amylopectin in the starch of different plants is different and is an important characteristic that determines the properties of starch in both grains and solutions. In addition, within the limits of one type of starch, noticeable oscillations of this ratio are observed [10].

On average, the starch contains 25% amylose and 75% amylopectin. By sorting, maize varieties are obtained, the starch of which contains 55-82% amylose. The waxy corn starch contains over 93% amylopectin.

Electron microscopy is used to study the internal structure of starch grains. First of all, it was established that there is no homogeneity in the grain structure. On the corners of the grains particles with a size of 4-10 nm were fixed [17]. Most authors conclude that the main organizational part of the structure of grains of starch is the radial fibrillar bundles of linear macromolecules [18-20]. Such a structure is concentrated in the middle of the annular sections of the grain. Fibrils diverge from the center outwards and cross the ring without an obvious rupture. The average thickness of the linear fibril is 0.1 μm [19]. It is shown that the tangential layering of grains is associated with periodic growth of grains [20]. Studies [21] have shown that in the core zone of the starch grain, mainly amylose is concentrated. Moreover, during the gelatinization [19] of the oxidative treatment, amylose is extracted from the grain for small grains of starch, the average volume of successive external layers of amylopectin corresponds to the volume of the core. X-ray scattering and birefringence fix the radial distribution of the layers by alternating blocks [22]. Taking into account the density, the degree of polymerization of the block was determined, it was (4 ÷ 6) x 105 [21]. It was suggested that a single block is a molecule of amylopectin. Along with the tangential orientation periods, the periodicity of the radial layers ~ 54 A was observed.

On the contrary, the authors of [23] did not observe concentric layers of starch in the analysis of electron microscopic images of the sections of starch grains, and there are also tangentially located layered regions. The authors concluded that the main organizational part of the structure of starch grains is radially located polysaccharide molecules and (or) radial fibrillar beams of these molecules.

The authors of [24] believe that the semi-microscopic radial structure of starch grains is more correctly characterized as a "folded micellar", rather than "micro fibrillar". The lamellar tangential structure of starch grains, in their opinion, is due to the alternation of high and low molecular fractions of amylose and amylopectin.

By analogy with cellulose, the authors of [25] believe that the starch micro fibril contains 7 elementary fibrils, but less lipid binders. This leads to the formation of empty capillaries, the presence of which explains the pronounced adsorption of water as a function of the change in air humidity. The proposed model is in good agreement with X-ray diffraction analysis, swelling, density measurement, and hydrolysis.

Starch granules have a microcrystalline structure and give two main types of radiograms: a type characteristic of starch of cereals, and a type "B" characteristic of tubers. Intermediate types are of type "C". The crystallinity of a large number of starch species was determined by X-ray diffraction analysis [26]. The degree of crystallinity averaged 14-19%. It was noted that in the crystalline region of cereal starches the structure of the "B" type was 10%, the rest was in the "A" type. Comparing the results of X-ray diffraction and electron transmission microscopy, the researchers [27] concluded that the alternating X-ray patterns reflecting the presence of amorphous and crystalline regions in the starch grains correspond to the "graininess" of the grain, recorded by electron transmission microscopy.

Starch, amylose and amylopectin insoluble in cold water. When heated in water, the starch grains are destroyed to form a gel (paste). Gelation of starch is a complex process, going in three main stages. First, the starch grains reversibly swell, attaching a small amount of water. When the temperature rises, a large amount of water is added, accompanied by a strong swelling of the grains with an increase in their volume by a factor of hundreds and an increase in the viscosity of the solution; this stage is irreversible. Swelling of starch occurs due to the breakdown of hydrogen bonds and hydration of macromolecules of polysaccharides. In the last step, the soluble polysaccharides are extracted with water, the grains lose shape, turning into pouches suspended in solution. This structure of the starch gel is the primary structure [28].

The authors of [29] using spin-spin relaxation time of protons of water molecules and biopolymer explain the mechanism of gelation through the formation of clusters of multinuclear complex compounds. At the first stage, clusters are formed, whose lifetimes are much shorter than the relaxation time of water molecules. In the second stage, stable clusters are formed, consisting of amylose macromolecules, whose lifetime is comparable or greater than the relaxation time of water. At the final stage, the clusters are combined into a single gel network.

Interesting and controversial is the question of the crystal structure of starch gels. A study of the effect on the spin-spin relaxation time of the system temperature and concentration [30] made it possible to detect a drop in this index during the initial heating period, which is especially noticeable at low concentrations. The results are interpreted by the authors as follows: the gelling process is similar to melting and represents the transition of partially crystallized starch to an amorphous state. As a result of the gelling process, there is an increase in the hydration and mobility of chains of macromolecules. In a later work, by methods of X-ray diffraction at large and small angles, the researchers [31] discovered disk-like regions with an increased electron density, which have the crystalline structure of the amylose β-form, in the gels of destructive starch. The degree of crystallinity of the gels was 16%. The authors believe that the sol-fractions of the molecule are hydrated, the double helices are formed during the dehydration of long segments of branched and linear molecules. Above the critical concentration, the double helices aggregate, forming crystalline nuclei, which grow into disk-like regions.

The combination of differential thermal analysis (DTA) and thermo gravimetric analysis (TGA) [32] established the endotherm city of the gelling process, which is attributed to the energy required to break the structure of the starch grains. The value of this energy is higher than the energy released by increasing the hydration of starch.

The diffusion of water in gels was studied by the method of nuclear magnetic resonance with a pulsating gradient field [33]. It was found that in gels all water molecules show the same differential properties as in pure water. The activation energy of the water molecule in the gel remains the same as for pure water. The self-diffusion coefficient is proportional to the square of the water content in the gel. Granules of swollen grains collapse is small, thus, are not a noticeable obstacle to the diffusion of water.

Investigation of structuring in model polysaccharide systems [34] allowed to draw a conclusion linking gelling with cooperative interactions between aggregated amyloses and linear segments of branched amylopectin. It is amylopectin that promotes amylose aggregation. Moreover, it acts as a precipitator, amylopectin is absent in the phase-depleted phase in the polymer-depleted phase, and in starch gels it participates as a filler of polymer-rich phase in the formation of a three-dimensional polymeric network [35]. The researchers established [36] that the intrinsic viscosity is determined by the structure-the ratio of the branched and unbranched portions, of the long and short chains, and not of their molecular weight.

From the above, it can be seen that starch is an extremely complex system. The composition and structure of such a system ultimately determines the properties of materials based on starch.

1.2. Theoretically, the fundamentals and practical aspects of obtaining starch modified by oxidation

Starch products have been widely used in various industries, for example, textile, food, paper, oil. This is due to the relative cheapness of starches, the reliability of raw materials and almost complete biodegradability. In the textile industry, starch and its derivatives continue to occupy a leading place in the scope of application as thickening and sizing preparations. According to the Swiss company "Beningen Corporation" for 1997, 75% of the world's production of sizing and thickening preparations is accounted for by starch and its derivatives [37]. At the same time, Western producers offer a wide range of modified starches: solvitose (Netherlands), solvitexes, CE imprints (Em-St, Germany), etc. In the USA, for example in industry, more than 700 thousand tons are annually used, and in Japan - about 200 thousand tons. modified starches.

In Russia, the development of modified starches was first organized by VNIIK, and currently only 10 of them are produced for different industries in the amount of 40,500 tones. per year, although the demand for them is about 150 thousand tons. per year [38].

Modification of natural starch can be carried out by chemical, physical, mechanical methods, and also by a combination of these methods [39]. Chemical modification should be understood only as processes that lead to chemical changes in macromolecules of starch. The chemical methods for the modification of natural starch include: oxidation, phosphating, recrystallization, crosslinking of macromolecules, inoculation of synthetic polymers, esterification.

The most known and widely used in the industry type of chemical modification of starch is oxidation [40, 41]. The purpose of the oxidation reaction is the partial oxidation of the hydroxyl groups that are present in the starch, various properties can be given to the starch to the carbonyl and carboxyl groups: increased solubility, good adhesion and skin-forming properties. The use of oxidized starch as a thickening agent in the textile industry makes it possible to increase the degree of fixation of active dyes to tissues. As a rule, the oxidation of starch results in a suspension, and the process is carried out at low temperatures (t = 20-30 °C) to avoid strong oxidative degradation of the starch macromolecules. During the oxidation of starch, a concentrated solution of the oxidant is introduced in several portions. This is done in order to avoid local concentrations of the oxidant, which can lead to excessive oxidation of starch on its surface and slowing down the diffusion to the interior of the grain. To carry out the oxidation reaction of starch, the following oxidizing agents are used: potassium permanganate ($KMnO_4$), hydrogen peroxide (H_2O_2), ammonium persulfate ($(NH_4)_2S_2O_8$), sodium hypochlorite (NaClO).

In the Russian industry, the technology of gelling potato starch, obtained by oxidizing starch with potassium permanganate, has been mastered for a relatively long time [42-44]. A solution of permanganate is introduced into the acidified starch-starting suspension. It is assumed that the oxidation of the starch grain starts from its surface, and then, due to the porosity of the starch grain, the oxidant diffuses into it. Thus, oxidizing starch, permanganate is reduced to Mn^{2+}. Starch, oxidized with potassium permanganate, is used in very large quantities in the production of ice cream.

Researchers [45, 46] have suggested using hydrogen peroxide to oxidize starch, when preparing clots based on it. Sodium carbonate was used as the catalyst. When sodium carbonate is used as the peroxide oxidation catalyst, decomposition of hydrogen peroxide and the release of oxygen occur, which oxidizes the hydroxyl groups of the starch to the carboxyl groups. It is shown that the use of these reagents in the oxidation of starch increases the stability of the clotting during storage, contributes to an increase in the degree of fixation of the dye on the fabric and the stability of the color to physical and mechanical effects. To increase the efficiency of starch oxidation with hydrogen peroxide, it was proposed in [47] to use metal salts (Fe^{2+}, Cu^{2+}, Co^{2+}). The use of metal salts as a catalyst for peroxidation made it possible to increase the fluidity of the oxidized starch paste, in comparison with unmodified starch. Starch, oxidized by hydrogen peroxide, has found wide application in the textile industry as sizing and thickening preparations, and also in the paper industry for sizing paper [43].

In [48], for the mild oxidation of starch, it was proposed to use the hydrogen peroxide derivative, ammonium persulfate, as an oxidizer. The advantage of this oxidant is that, in the presence of various additives, it is possible to create mild conditions for the oxidation of starch without breaking the macromolecules. Ammonium persulfate has a higher redox potential than hydrogen peroxide. The scheme for the reaction of starch oxidation with ammonium persulfate in the presence of a catalyst (Fe^{2+}, Co^{2+}, WO_4^{2-}, Mn^{2+}, $Cr_2O_7^{2-}$) can be represented as:

$$S_2O_8^{2-} \rightarrow 2SO_4^{-}$$

$$Mn+ + 2SO_4^{2-} \rightarrow M^{n+1} + SO_4^{2-}$$

$$M^{n+1} + \text{starch} \rightarrow M^{n+} + \text{modified starch}$$

Oxidized starch is white. The viscosity values of the oxidized starch samples obtained are higher than that of native starch, but lower than that of unmodified starch. The influence of ultraviolet irradiation during the reaction of starch oxidation with ammonium persulfate has an insignificant effect on the change in the degree of oxidation. Starch, oxidized with ammonium persulfate, is used as a thickening agent when printed with active dyes.

The most commonly used oxidizer in the industry for the oxidation of starch is sodium hypochlorite. For the oxidation of starch with hypochlorite, a suspension of starch grains is treated with a solution of alkaline hypochlorite. After completion of the reaction, the suspension is neutralized with an acid. The properties of oxidized starch are related to the degree and type of treatment, and are also determined by the reaction conditions. The reaction parameters include temperature, pH, starch concentration, hypochlorite, the presence of organic and inorganic impurities [49.50]. Oxidized hypochlorite starch, supplied to the consumer, has the form of grains. The most characteristic feature of this starch is its whiteness.

In a number of studies [51-53], the dependence of the properties of oxidized starches on the surface structure of starch grain was investigated. During oxidation, part of the anhydroglycose units of starch is carboxylate, and some hydrolyses. Oxidation affects the surface structure of starch only at an active chlorine concentration of ~6%. As the degree of oxidation increases, the solubility of oxidized starch decreases. Oxidized with hypochlorite, starch gelatinizes much faster and at lower temperatures, and the viscosity of the paste increases more slowly than in unmodified starches [54].

A number of authors [53, 54] found that with an increase in the concentration of active chlorine, its consumption in the reaction and the concentration of carboxyl groups in the starch increased. The rheological properties of the oxidized starch glues are studied using a rotational viscometer at a shear rate of 1562-702.3 s-1. Clusters before and after oxidation of starch showed non-Newtonian thixotropic properties. In industry, starch, oxidized by hypochlorite, is used for the pigment coating of paper and as an adhesive in the paper industry, as well as in the textile industry for the preparation of sizing preparations for sizing various yarns of artificial silk, synthetic fibers and mixtures thereof [55].

1.3. The use of modified starches and their compositions

The most common among the modified starches used as thickeners are the starches obtained from the esterification reaction. These starches are characterized by improved solubility, increased stability of their aqueous solutions and facilitated their wash ability from tissue [56].

Carboxymethyl and hydroxyethyl esters of starch are used which not only rapidly dissolve in water and are resistant to acidic medium, but also penetrate into the tissue, are well washed off from it, provide a high degree of fixation of dyes on the fiber. Based on carboxymethyl ether, starch is produced under the brand of solvitose C5, and on the basis of hydroxyethyl ether - solvitose H4M. In starch ethers, printing and technical properties are better than esters, and therefore they are used mainly for printing inks [57, 58].

Solvitose C5 is used for printing fabrics from natural and chemical fibers with dispersed and dye dyes. It forms highly viscous thickeners and is used in the form of 5-10% solutions. The disadvantage is the interaction with salts of 3 valence metals, passing with the formation of precipitation [58].

In [59], starch acetate, CMC, and oxidized guaran were studied as thickeners. It has been found that when using starch acetate thickeners when printing with active dyes, the degree of fixation of the active dye is not inferior when using thickeners based on alginate. Especially bright color is obtained when using starch acetate.

Currently, there is a large number of different brands of solvitose with a targeted modification, for example, Kviksolan RES, used in recipes for printing velvet, corduroy velvet fabrics. It provides easy flushing and low weight gain. Solvitose R5 - thickener for printing with active and disperse dyes in cotton and blended fabrics [60].

The thickened monogum N and W are readily soluble in water with the formation of alkaline solutions (pH = 10). They are resistant to electrolytes and are unstable to salts of polyvalent metals. The monogum W is used alone, as well as in combination with other thickeners and when printing fabrics with cubes (for one-stage and two-stage printing), cubosolic, phthalocyanine dyes and diazo compounds [61].

The thickeners of the prints S and R are readily soluble in cold water and have an anionic character. Printex S is designed specifically for printing fabrics from synthetic fibers, especially polyacrylonitrile. Printex R - is intended for printing fabrics containing cellulose fibers.

The thickener colloprint SM, produced by the company "Avebe" (the Netherlands), easily soluble in water has a high yield of the dye and is successfully used for printing with cubes and cubesolts, as well as for standby printing [62]

The company "SNT" on the basis of starch produces thickeners for general use: it is inherent in T, it has ST, high viscosity and neutral thickener is inherent in AB, intended especially for printing silk and woolen fabrics from synthetic fibers [63]. Almost all thickeners based on starch esters have slightly alkaline properties, so they are resistant to bacteria.

From the products of starch degradation, the following are used as thickeners: dextrin’s, British hums, diatheses [64]. Unlike conventional starches, they are more ductile and fluid enough, which are less sensitive to the presence of acids and salts, metals.

However, in pure form, a dextrin thickening is used extremely rarely due to high adhesion and hygroscopic agent. As a rule, a mixture with starch and tragic thickeners is used. As a thickener, 30-50% solutions of dextrin and British gums or diatex are used, both alone and in mixture with other thickeners when printing fabrics with vat dyes [61].

It was suggested in [65-67] to use modified starch for printing with vat, active and azo dyes. Modified starch was obtained by thermal treatment (t = 160-170 °C) of a mixture of corn starch with orthophosphate or sodium three polyphosphate and urea. The resulting phosphate starch was tested in laboratory and production conditions when printing with various classes of dyes. However, this thickener is of greatest interest for vat and azo dyes. The disadvantage of this thickener is its sensitivity to microbiological degradation.

Thickeners of solvitose A8, solvitose R5 and monogum N are obtained on the basis of carboxymethyl starch. Their production is connected with a complex chemical synthesis. As for the quality of printing, these products do not exceed such a classic thickener for active dyes, like sodium alginate, but they are not inferior to it. All these thickeners are imported and therefore quite expensive and scarce. Several enterprises already use thickeners, not only on the basis of starch derivatives, but also on the basis of compositions with water-soluble polymers. It was shown in Ref. [68] that when using thickeners based on polyacrylamide, saponified polyacrylamide, starch with grafted polyacrylamide and carboxymethyl starch

(CMC) when printing with active dyes, the printing results are the same as for thickeners based on alginate. It was found that with the use of the listed thickeners, the purity and brightness of the printed patterns obtained are close to the results of printing the thickeners based on starch with grafted polyacrylamide, but it turned out to be tougher than using polyacrylamide and saponified polyacrylamide. In work [69], it was established that polymer compositions based on rice starch and phosphorus-containing oligomer, possible purposeful use of them both in the sizing process and as a thickener when finishing cotton fabrics with active and cold dyes. The introduction of starch and a phosphorus-containing water-soluble oligomer based on poly phosphoric acid and a, g-dichlorohydrin glycerol into the composition completely eliminated the alginate from the recipe.

In [70], a composition based on hydrolyzed acres of emulsion and starch was adopted as a thickener.

The polymer composition containing starch, hydrolyzed acrylic emulsion, HYPAN and PAA is characterized by higher values of the degree of thixotropic reduction of bonds that were destroyed by mechanical action as a result of random successful collisions of particles in Brownian motion, and the system is more stable.

CONCLUSION

From the foregoing, it can be concluded that the thickeners used based on starch or its derivatives do not provide complete information about them. In this aspect an important role is played by the notion of the essence of the modification process, especially with oxidants, because of the poor knowledge and application of oxidized starch derivatives or compositions based on them as a thickener for printing with various classes of dyes.

CHAPTER II. METHODICAL PART

2.1. Characteristics of the objects of study

Technical rice starch - white powder. Mass fraction of the main substance up to 85% gluten content 5-6% moisture mass fraction 6-7%, in the cellulose and sols up to 4%

2.2. Characteristics of used chemical materials

The work used substances whose purity was controlled by boiling and melting points, refractive indices, and also by the spectral method [71,72].

Technical sodium hydroxide - (GOST 2263-71) - scaly mass (in solid form), grade TR; $T_{liq.}$ = 322К, $T_{boil.}$ = 1385К; is dissolved in water, ethanol, methanol.

Unifloc - water-soluble polymer preparation according to (TU Uz 6.1-43-95) is a powder of yellow, cream and pink color. The mass fraction of water in it is not more than 10%, the undissolved product is not more than 5%. Unifloc acts as a weak alkali. Its aqueous solutions help to reduce water loss and stabilize clay solutions, to precipitate suspended particles in sedimentation tanks and water storage facilities, to filter and deposit various pulps.

HYPAN is a liquid, slightly yellow in color, the mass fraction in the commercial product is 80%, TU Uz 61-29-94 rev. № 1.

2.3 Mechanical treatment of water-polymer system in the process for producing modified starch compositions

Composite modification of starch was carried out with the treatment of starch with an oxidizer on its base with a unifloc and HYPAN thermostat, in which the treated mixture was subjected to mechanical action until a homogeneous mixture was obtained at a temperature range of 50-60 ° C of the gelatinization temperature of the oxidized modification of starch. The process is carried out at different ratios and at different temperatures.

2.4. Method of skin formation

Skins were obtained from polymer solutions by evaporation of a solvent [73]. The polymer solution was poured into a flat cuvette measuring 30 * 22 * 0.5 cm, made of polished silicate glass with surface purity of 7.

In determining the optimum concentration of skin-forming solutions, their viscosity, filterability and the ability to spread over the cell surface were taken into account. It has been experimentally established that 5-10% solutions of the selected polymers in water are most suitable, which were used for the preparation of skins. The influence of the temperature conditions for the preparation of skins was studied using the example of modified starch at the initial evaporation temperatures of solvent 298 and 318 K. Evaporation results showed that their mechanical characteristics do not differ within the experimental error.

The solutions, pre-filtered under pressure through a glass filter of Schott No. 2, were poured into a thoroughly cleaned cuvette, set horizontally on a glass table. The amount of solution was such that the thickness of the finished skin was 60-100 μm. The cuvette with the solution was placed in an air thermostat, in which freshly-chalked calcium chloride was used to purify the air. Before evaporation of the solvent, the cuvette with the solution was covered with clear glass and left for 4-5 hours to uniformly spread the solution over the surface of the cuvette. After that, the glass was raised, leaving a gap, different solutions were selected depending on the boiling point of the solvent. It was the smaller the lower the boiling point of the solvent and the more homogeneous skins were obtained.

The solvent was evaporated at a temperature of 298 K to a content of 15-20% in the skin for two days. The resulting skin was then taken out of the cuvette and cut into slabs of 4.5 * 0.6 cm in size to allow evaporation of the solvent. Further drying was carried out in a vacuum cabinet at a residual pressure of 10^{-2} mm Hg. column and a stepwise increase in temperature from 298 to 373K. At each temperature step, the skin was held to constant weight. At all the drying stages, the amount of remaining solvent in the skin was controlled by the loss of weight of the control solution prepared in a bag with an exact sample of the polymer.

2.5. Methods for determining the rheological properties of compositions

Method for determination of viscosity

The viscosity of the polymer compositions was determined according to the procedure described in the literature on the "Rheotest-2" device [74]. The research was carried out in the laboratory of JV "Textile Spectrum Color". The measuring device of the device is a system of two cylinders:

a) a movably loaded cylinder;

b) a rotating cylinder.

The inner cylinder is a measuring cylinder. The driving mechanism of the cylinder measuring device is 12 speeds. In the measurement, the analyze is located in the annular gap between the inner and outer cylinder. The rotating inner cylinder is connected through a measuring shaft with a helical spring, the deviation of which is proportional to the rotational torque acting on the inner cylinder. The tangential stress arising in a viscous system is determined by the formula:

$$\tau = \frac{M}{2\pi r^2}$$

M - the torque of the link of the spring;

R - is the radius of the inner cylinder, mm;

Gradient of shear rate:

$$\dot{\gamma} = \frac{\omega \cdot r^2}{R^2 - r^2}$$

ω - is the angular velocity of the inner cylinder, rad;

R -is the radius of the outer cylinder, mm;

r - is the radius of the inner cylinder, mm.

The values of gradients of shear rates are given for each rotational speed of the measuring cylinder. Knowing τ and $\dot{\gamma}$, we can calculate the viscosity η in Pa · s for all velocities of the measuring cylinder.

$$\eta = \frac{\tau}{\dot{\gamma}}$$

Method for determining the degree of thixotropic reduction

The degree of thixotropic reduction was calculated by the formula:

$$p = \frac{\Sigma \eta_{обр}}{\Sigma \eta_{прям}} \cdot 100,\ \%$$

$\eta_{stra.}$ – вязкость загустки при увеличении нагрузки;

$\eta_{rev.}$ – вязкость загустки при постепенном снятии нагрузки.

2.6.Physico-chemical methods of studies of fogging systems

Determination of physical and mechanical properties of skins of polymer systems.

The aim of the paper is to determine the strength and relative elongation of skins at different tensile speeds. The work is carried out on a machine for testing textile materials RT-250M-2 in the **CCL JV "Textile Spectrum Color"** [75]. The machine is a device for stretching fibers and skins with a visual reading of tensile forces and elongations.

To do this, six parallel samples are selected from each skin in the form of a double-sided spatula with a working section 25 mm long, 10 mm wide with a total length of 75 mm. In the samples, the working section is marked, the length and width of the sample are measured. Before testing, the samples are kept in a desiccator with a relative humidity of 65% for 24 hours. After that, the samples are tested on a tensile machine at speeds of 30, 60 and 240 mm / min.

Methods of microscopic research

Optical microscopy

The Nikon microscope is designed to produce an enlarged image of textile fibers, yarns, yarns and other textile materials.

Preparations for direct microscopic observations were prepared according to a known method [76]. Microscopy prepares drugs to examine the appearance of the fibers in order to study the smallest details of their structure in the longitudinal direction, to examine the cross sections of fibers and filaments in order to study the smallest details of their structure in the transverse direction, to measure the cross-sectional area of the fibers. For this purpose, a method of preparing a cross-sectional preparation using a hand microtome LS-113 is used. The investigated object is treated with glycerin or xylene to obtain a solid mass and is clamped into the microtome clamp so that the upper part of the object protrudes slightly above the clamp. The upper part of the object protruding above the clip is manually cut by the razor of the microtome level with the clamping plane. The resulting preparation is placed between two slides and studied under a microscope. On the lenses and eyepieces there are figures that indicate the degree of increase of the object under consideration; the product of the integers of the objective and the eyepiece gives a general increase.

Investigation by IR spectroscopy

Infrared spectroscopy studies were performed using a MAGNA-IR 560 spectrometer [77].

CHAPTER III. DISCUSSION OF THE RESULTS OF THE EXPERIMENTS

3.1. Selecting a component for creating thickening compositions

For the implementation of profound structural transformations, the development of the industries of our Republic, the overcoming of the one-sided raw material orientation acquires decisive importance. In this regard, profound changes quickly entered into our science. The current stage in the development of chemistry and technology of composite materials is of great importance for a fundamental shift in the national economy, and especially in the textile and light industry in the process of finishing cotton fabrics.

Proceeding from this constantly growing requirements for the quality of textile materials necessitate the search for new polymer compositions that are promising for use as efficient textile auxiliaries and dyes. At the same time, one has to take into account the main factor, which is that new compounds and preparations based on them should be more efficient than existing ones at lower consumption rates, their production should be safe and affordable, and the waste products of finishing industries with their application should be environmentally friendly. Thickening materials play an auxiliary role in textile production, nevertheless, their cost and quality significantly affect the economic performance of finishing production, and improving its technological properties creates the prerequisites for reducing the cost of printing by increasing the degree of useful use of the dye. Many textile enterprises with active dyes no longer use native starch, and expensive imported thickeners are used, which significantly affects the price of the product and causes the connectedness of production, with their delivery spending not only a lot of time, but also the foreign exchange reserves of the state.

At present, acrylates of various structures, as well as derivatives of cellulose and, to a lesser extent, starch derivatives, dominate the binders and thickeners abroad. In this case, binders and thickeners should have a high adhesion to the fibrous material, and also produce homogeneous solutions, which is especially important when printing with mesh patterns. No less difficult task is to identify the optimal structure of polymers having a high thickening power. In this case, the thickener should be rheological and thixotropic properties close to traditional alginate thickeners.

Starch is by no means an ideal thickener, since the thickener based on it is unstable when stored and has a low elasticity. Blanks based on starch are sensitive to the action of acids, alkalis and metal salts, poorly penetrate into the thickness of the fiber and difficult to wash off the fabric after printing. They give a poorly drying, rigid, non-plastic and water-insoluble skin, which makes it difficult to wash the fabric after printing and can lead to the formation of "layers" on the fabric during washing. In addition, the remaining after rinsing of the thickener imparts to the fabric stiffness and surface fixation of the dye, which reduces the resistance of the stains to friction [78].

The wide use of starch and its derivatives in the textile industry, in particular as thickening materials during printing, makes it urgent to search for new routes for its chemical, physical and combined modification.

Since no single polymer can be used as a perfect thickener, it is possible to create light-weight (technological) coatings for textile materials on the basis of polymer compositions. Therefore, a very urgent task is to develop the composition and formulation of effective compositions based on local polymeric raw materials of both natural and synthetic origin, suitable as a thickener in the process of finishing cotton fabrics.

One way to solve the above problems is to obtain starch preparations with valuable properties, converting it from a compound containing one type of functional groups to a compound containing different types of functional groups. In this regard, of great interest is the bunches prepared by chemical oxidation of starch with sodium chlorate. In this process, the viscosity of the starch decreases. To increase the viscosity and plasticity, synthetic water-soluble polymers are added as rheological modifiers.

The choice of rheological modifier is determined by the formulation of the water-dispersion system, its purpose and application conditions [79]. The obtaining of new rheological modifiers with a set of necessary properties is possible in two ways: 1) the synthesis of new polymer materials and the development on their basis of new effective preparations for finishing production, as well as efficient technologies; 2) development of effective multicomponent polymeric systems based on large-capacity polymers or their analogs, for the production of which no significant changes in the available technologies and equipment are required.

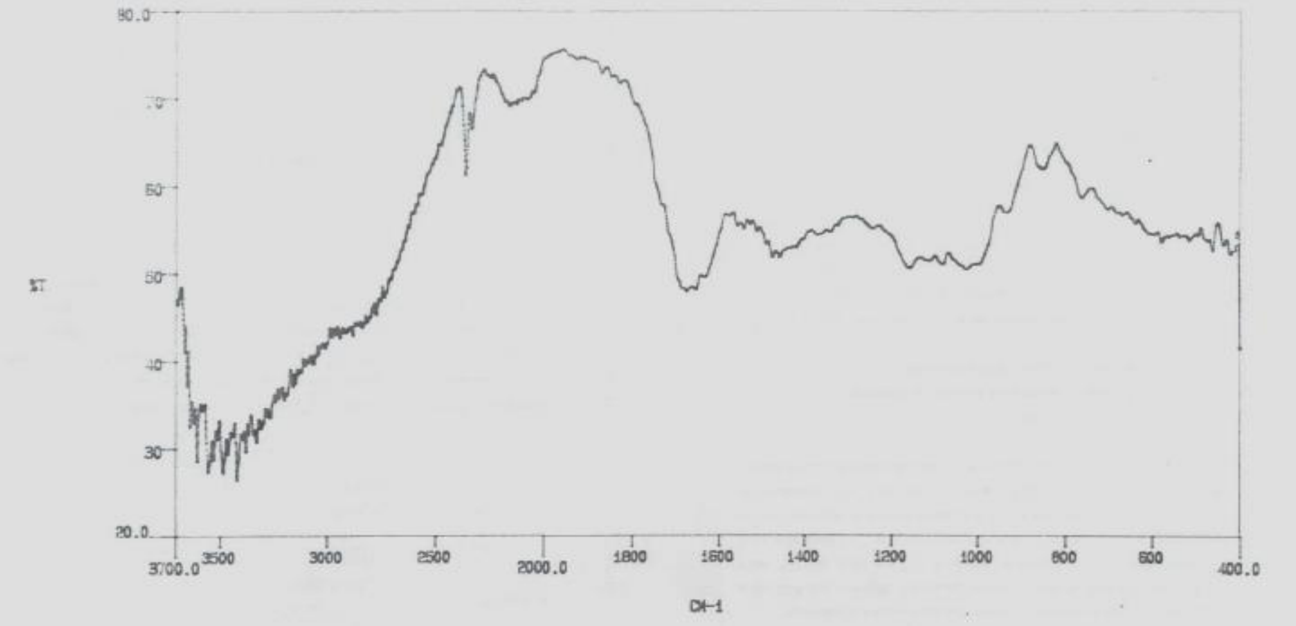
The choice of a rheological modifier is determined by the formulation of the water-dispersion system, its purpose and application conditions. Wide use of cellulose thickeners is provided by their good rheological properties, sedimentation resistance. By varying the degree of molecular substitution, the molar mass of the cellulosic polymer, controlling uniformity in substitution, it is possible to achieve complete and rapid solubility of the cellulose ether in both hot and cold water, as well as very high bio stability. The action of cellulosic thickeners is particularly effective in alkaline or near neutral environments, although solutions of many cellulosic (nonionic) polymers undergo very slight changes in viscosity in the pH range of 2-12. It should also be noted that solutions of cellulose thickeners are fairly stable in the presence of inorganic electrolytes of high concentration. Of cellulose thickeners, methylcellulose, hydroxyethyl cellulose and the sodium salt of carboxyl methyl cellulose (CMC) are most often used. But for the production of CMC or other listed cellulose derivatives we are dependent on chemical reagents. In this connection, it seems interesting to investigate the possibility of using as water-soluble synthetic polymeric preparations Unifloc and HYPAN as a modifier.

It is assumed that by creating compositions of synthesized oxy starch with synthetic water-soluble polymers, it is possible to obtain sufficiently plastic thickeners with the required viscosity. As a synthetic rheological modifier, a polymeric substance of the acrylate type, unifloc, was produced in our republic at OJSC "Navoiazot". The choice of this highly alkaline component and its use as a synthetic rheological modifier is due to its environment that meets the requirements for use with active dyes and also very well solubility in water forming a highly structured gel fluctuation grid having hydrophilic groups in their composition that form hydrogen bonds like chemically oxidized starch, and water-soluble poly-acrylates.

3.2. STUDY OF OXIDIZED STARCH AND COMPOSITIONS BASED ON ITS METHOD OF IR SPECTROSCOPY

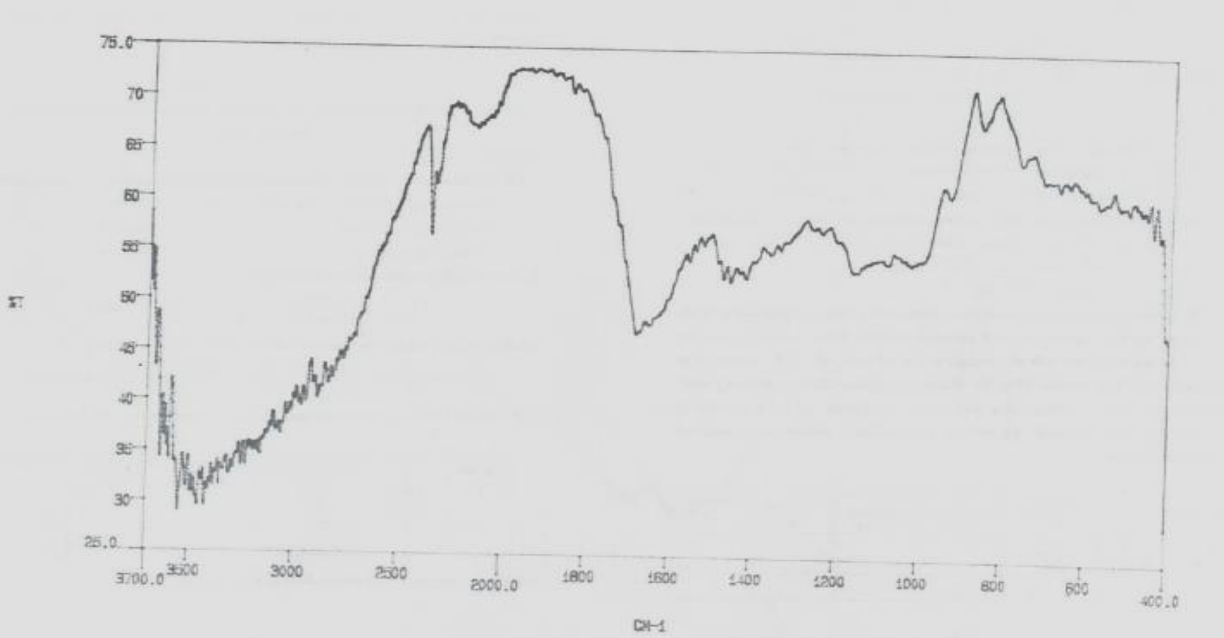
Starches also carbohydrates (polysaccharides) with the general formula ($C_6H_{10}O_5$) and their spectra have similarities basically similar to the spectra of cellulose [80]. When studying the spectrum of modified starch, the spectra of native rice starch, obtained from rice husk, were first removed. In the spectra of starch (Pic. 1a), one broad band is observed at 3500-3200 cm^{-1}, which is characteristic of stretching vibrations of hydroxyl groups of polymers. In the interval 1200-1300 cm^{-1} there are folded bands related to the stretching vibrations of the ether and hydroxyl group C-O; there are also bands in the region of 930 cm^{-1} characteristic for α -1,4 polysaccharides (starch).

The bands in the region of 3644 cm^{-1} and 2939 cm^{-1} are due respectively to stretching vibrations of the OH and CH_2 group, and the band 1673 cm^{-1} is likely to be related to the deformation vibrations of the crystallization water. Absorption in the region of 1472-1200 cm^{-1} can be attributed to the scissors and external deformation vibrations of CH_2, and also due to plane oscillations of hydroxyl groups. In the range 1000-1200 cm^{-1}, the frequencies of C-C and C-O bonds of ring structures and deformation vibrations of the CH_2 groups lie. The bands 760, 851 and 940 cm^{-1} can be attributed to external deformation vibrations of CH_2 and CH groups and to the pulse oscillations of pyranose rings [81].



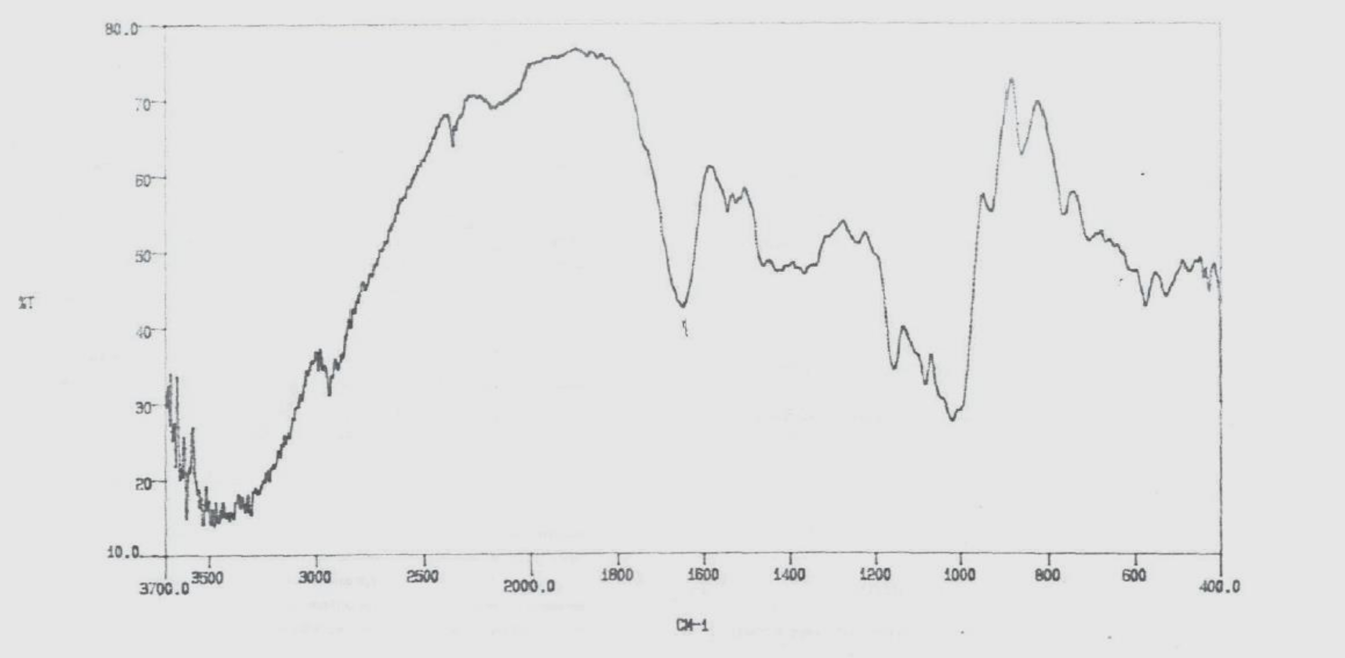
Pic.1. IR spectrum of natural rice starch

It is known from the literature that, in addition to the absorption bands common for all starches in the indicated regions, spectral features were revealed in the spectral range 840-860 cm^{-1}, depending on the origin of this starch. For rice starch, which we are investigating, this region is equal to 860 cm^{-1}, which is 62.74% (Pic. 1). But when starch is modified with oxidation with sodium chlorate, this region is equal to 847 cm^{-1}, the intensity of absorption decreases to 61.8%. A characteristic peak appears in the 1690-1720 cm^{-1} region, for the carboxyl group carbonyl (Pic. 2). This is absent in the IR spectra of conventional starch.



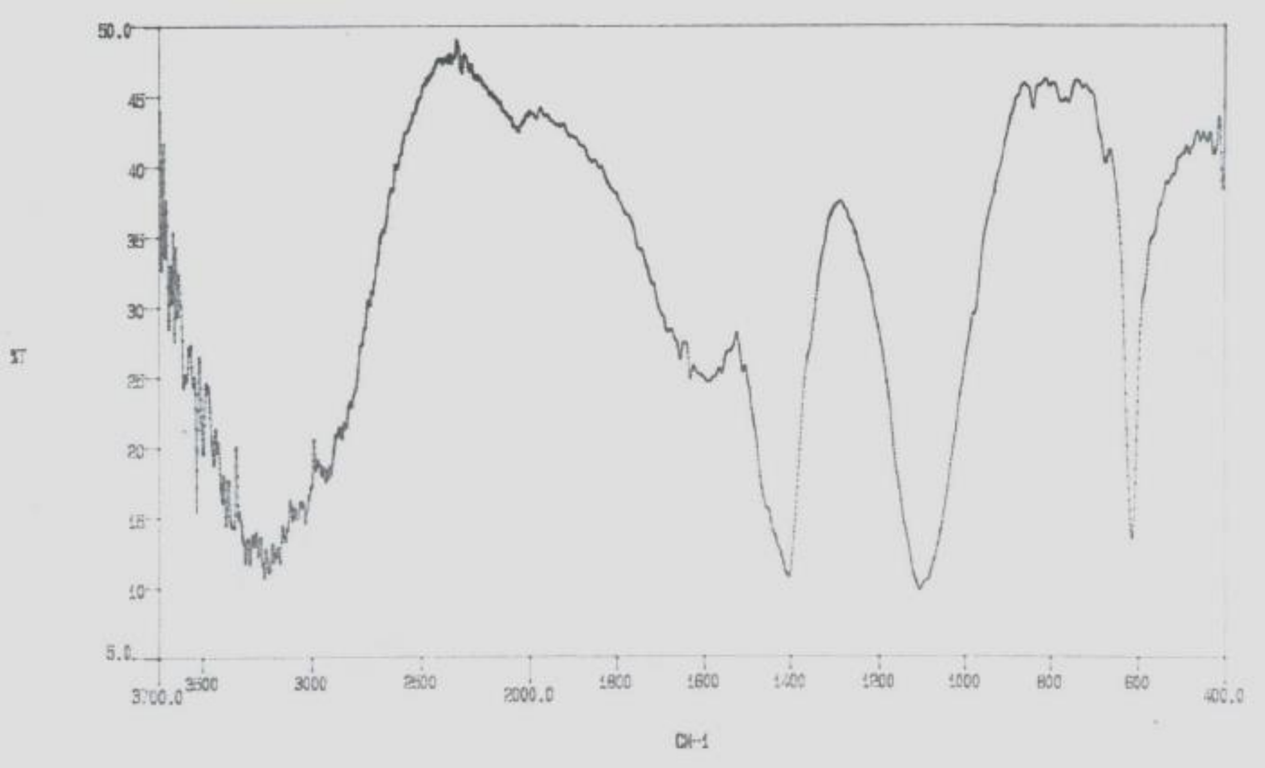
Pic.2. IR spectra of modified rice starch oxidized with sodium chlorate

From the literature it is known that in the spectra of carbohydrates in the region of 1300-1500 cm^{-1}, the frequencies of the deformation vibrations of the CH_2 groups manifest themselves, and a band-specific band of bands is observed (in decreasing order of intensity) [77]. In the spectrum of starch of rice husk this absorption region in the region of 1428 cm^{-1}, in the spectrum of modified starch, this region is observed at 1440 cm^{-1}. But in compositions of modified starch with HIPAN (Pic. 3), these spectra are mixed and the intensity of absorption increases in the regions of 1415 and 1383 cm^{-1}. This is probably due, in particular, to interactions between the CH_2 groups and the environment, which lead to a significant change in the frequencies of the methylene groups, depending on the conformation of the CH_2OH groups.



Pic.3. IR spectra of oxidized starch compositions with HYPAN

Also in the spectrum of Pic. of the region 1650-1640 cm^{-1}, two peaks appear that are associated with the amide groups. In the 1703 cm-1 region, a characteristic peak appears for structures with a hydrogen bond between the carboxyl and amide groups [82]. In the spectra of many sugars, a number of bands in the region 2600-2800 cm^{-1} are also observed. But in our case, the blurred character of these bands does not give grounds for classifying them as overtones or composite frequencies. Absorption in this region is characteristic for compounds with OH groups included in a very strong hydrogen bond of chelate type. The absorption bands of stronger hydrogen bonds are largely overlapped by the absorption bands of the CH, CH_2 and CH_3 groups located in the 2800-3000 cm^{-1} region. In addition to increasing the number of components, the spectra of this region decrease in intensity (Pic. 4).



Pic.4. IR spectra of oxidized starch, HYPAN and unifloc compositions

Comparison of the spectra (Pic. 1, Pic. 2) of the controls with the compositions (Pic. 3, and Pic. 4) shows that the change in the spatial arrangement of even individual hydroxyl groups or their replacement leads, as a rule, to a noticeable change in the entire system of hydrogen ties. It should be noted that when the alkaline medium increases, the characteristic peak in the region of 1710 cm^{-1} proves that hydrogen bonds between the carboxyl groups and the amide group are present in the compositions.

It can be concluded that the spectrum of starch of rice husk is characterized by the presence of an absorption band of 2988-2360 cm^{-1}. In modified starch, the intensity of these peaks increases. Adding HYPAN and unifloc, the intensity of the absorption of these bands again decreases. Probably, a weak hydrogen bond is formed in the composition.

3.3. STUDY OF THE RHEOLOGICAL PROPERTIES OF WASHING COMPOSITIONS ON THE BASIS OF OXIDIZED STARCH AND WATER-RELATED POLYMERS

Tens of brands of modified starches are offered to textile enterprises as thickening agents: solvitose (Netherlands), solvitexes, CE emprints ("EmSt", Germany) imported from other countries at the expense of currency [83,84]. Thickening materials play an auxiliary role in textile production, nevertheless, their cost and quality significantly affect the economic performance of finishing production [85].

At domestic textile enterprises, because of the lack of their own assortment, either expensive imported modified starches or a clot based on alginates are used [86]. In addition, it is not only a great economic cost, but a lag in the technology of obtaining effective thickeners based on our own raw materials for several years even decades [87]. In connection with this, we have studied the possibility of their complete or partial replacement by drugs on the basis of raw materials and products of domestic production.

Of the new types of mixtures that can be used in printing, mention should be made of polymer-composite thickeners based on natural and synthetic water-soluble high-molecular compounds. Of these, the polymer compositions containing oxidized starch (OK), with sodium chlorate, as well as water-soluble polymers such as HIPAN (hydrolyzed polyacrylonitrile), poly acrylamide (PAA) and unifloc (UFC), which are domestic products.

We have studied the changes in the viscosity of aqueous solutions of the compositions. The results of the data obtained are presented in Table 1. As can be seen, the concentrations of the components have a significant influence on the viscosity of the polymer composition solution from the data obtained. The sharp increase in the viscosity of the aqueous solution of the composition appears to be due to the acceleration of the process of decomposition of the oxidized starch in the presence of composition in the HYPAN composition on the one hand, and the other side between the starch and the unifloc is the structure formation of the molecules leading to an increase in the viscosity of the solution.

Table 1

The change in the viscosity of aqueous solutions of the oxidized starch composition depending on the composition of the composition at various temperatures

Consist of composition, %			Viscosity of solution, Pa.c	
Oxidized starch	Unifloc	HYPAN	Temperature, K	
			298	313
6,0	-	-	0,98	0,84
6,0	-	-	1,05	1,02
7,0	-	-	1,22	1,17
8,0	-	-	1,29	1,23
5,0	0,55	0,06	1,47	1,39
	0,60	0,08	1,59	1,51
	0,65	0,1	1,68	1,62
	0,70	0,12	1,81	1,73
6,0	0,55	0,06	1,77	1,67
	0,60	0,08	1,89	1,83
	0,65	0,1	2,03	1,94
	0,70	0,12	2,15	2,07
	0,55	0,06	1,94	1.86

7,0	0,60	0,08	2,10	2,03
	0,65	0,1	2,26	2,18
	0,70	0,12	2,43	2,35

Polymer compositions, when dried, can form strong and elastic skins. The ability of the composition to skin formation is extremely necessary for thickening, as a result of this, the formation of skin bonds between the fibers, which contribute to a greater effect between the fibers, which in turn increases the endurance of the yarn in processing.

The quality of the skins is characterized by physical and mechanical properties that determine the physical and mechanical properties of the printed yarn, and therefore should not be worse than yarn [88,89].

These values of the yield stress and the degree of thixotropic reduction of the solutions of the compositions are shown in Table 2.

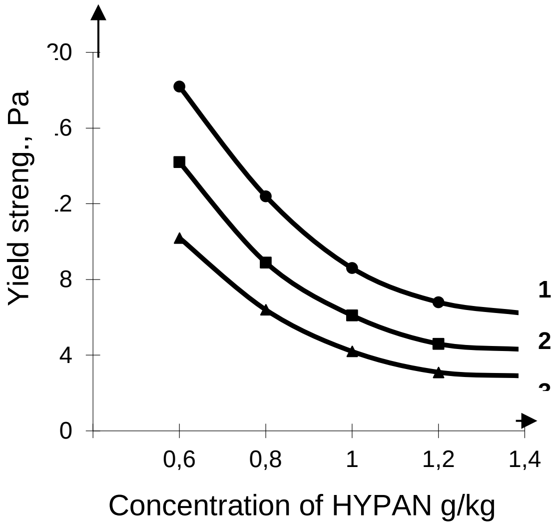
Table 2

Yield strength and degree of thixotropic reduction of compositions

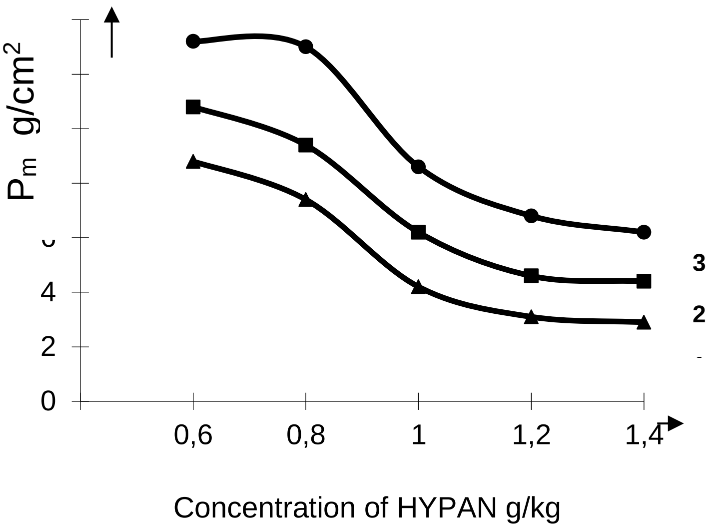
Content of components in solutions				Yield strength, g/cm^2	Degree of tick-solo recovery,%
OS, %	UFC, %	HYPAN,%	PAA, %		
6	-	0,06	-	62,55	87,43
	-	0,08	-	48,84	89,88
	-	0,1	-	37,18	90,21
	-	0,12	-	33,27	92,48
	0,55	-	-	39,77	93,28

6	0,60	-	-	30,43	94,34
	0,65	-	-	26,32	96,76
	0,7	-	-	17,55	96,62
6	0,55	-	0,1	27,34	79,85
	0,60	-	0,1	23,37	83,74
	0,65	-	0,1	17,70	85,24
	0,7	-	0,1	13,73	87,51
6	0,55	0,06	-	42,55	96,27
	0,60	0,08	-	33,17	97,71
	0,65	0,1	-	27,44	97,07
	0,7	0,12	-	19,47	98,33
6	-	0,06	0,1	23,32	87,53
	-	0,08	0,1	16,55	90,68
	-	0,1	0,1	12,33	91,37
	-	0,12	0,1	5,77	93,29
6	0,55	0,06	0,1	19,43	96,27
	0,60	0,08	0,1	11,88	97,72
	0,65	0,1	0,1	10,77	97,07
	0,7	0,12	0,1	2,11	98,33

It can be seen from the table that the yield stress with increasing content of UFC and HYPAN increases especially markedly. The yield strength of the composition increases when the composition simultaneously includes oxidized starch, HYPAN, PAA, and a rectilinear portion of the flow curve corresponding to the conventionally elastic region of the modulated elasticity and viscosity elastic consequences.



Pic.3. Dependence of the yield strength of the composition on the concentration of HYPAN. Thickeners based on:
1- OK - PAA - HYPAN;
2 - OK - UFC - HYPAN;
3 - OK - UFC - PAA - HYPAN



Pic.4. Dependence of the plastic strength P_m of the secondary structure of the polymer composition on the concentration of HYPAN. Thickeners based on:
1- OK - PAA - HYPAN;
2 - OK - UFC - HYPAN;
3 - OK - UFC - PAA - HYPAN

As studies have shown, when studying the dependence of the yield point (P_m) of a water-soluble polymer composition, very positive results are obtained for a plug based on a mixture of oxidized starch (OC), unifloc, HYPAN and PAA. These data are presented in Figures 3 and 4. We see a smooth course and the absence of minima on the curves of the dependence of Pm on the composition of the composition, which indicates that the thickeners are compatible independently, both from their ratios in the mixture (curve 1) and from additives and components of the printing ink (curve

2). The presence of good compatibility is also confirmed by the high stability of the mixtures obtained.

The results of the studies further show that, according to the nature of the rheological curves, a starch paste without HYPAN and unifloc can be referred to as elastically brittle or elastically brittle solid systems to describe their structural and mechanical properties that use characteristics such as elastic moduli and viscosity of elastic effects.

From the curves of the flow of 6% starch pastes and the polymer composition it follows that when the composition of the HYPAN and UFC is added to the composition, the elastic viscous solid system of the 6% modified starch paste is converted to an elastic-plastic system.

3.4. The process of formation of supramolecular structures in lightening compositions based on oxidized starch and water-soluble poly acrylates

It is known that the color characteristics of cotton fabrics and products based on them are of great importance. A decisive influence on the coloristic properties is rendered not only by the dyes, but also to a great extent by the conditions for the application of printing ink to the fabric and the processing of the fabric after printing, and the thickeners used are of no less importance. The latter, in turn, depends on the chemical nature and physico-chemical parameters of the thickener for printing [90]. At present, in the textile industry of our republic, thickening materials imported from abroad are mainly used [91]. They sometimes have a fairly high cost, which significantly affects the cost of production. Hence, scientific practical development of highly effective thickening compositions based on local, available raw materials is of no small importance.

As a result, complex scientific and applied research has been carried out to prove the possibility of successfully solving this problem and creating compositions as a thickener with given properties and structure. Such a composite is developed on the basis of oxidized-modified starch (OMS) sodium chlorate, unifloc and hydrolyzed polyacrylonitrile (HYPAN). The optimum composition of the compositions was established, the most important properties of which meet the existing production requirements [92]. The developed thickening composition of OMS-UFC-HYPAN possesses good physicochemical parameters. By dissolving this composition in water, skins were prepared in various embodiments and proportions of constituent components. The physical and mechanical characteristics of the skins obtained are presented in the table.

Table

Physic mechanical properties of a skin of polymer compositions

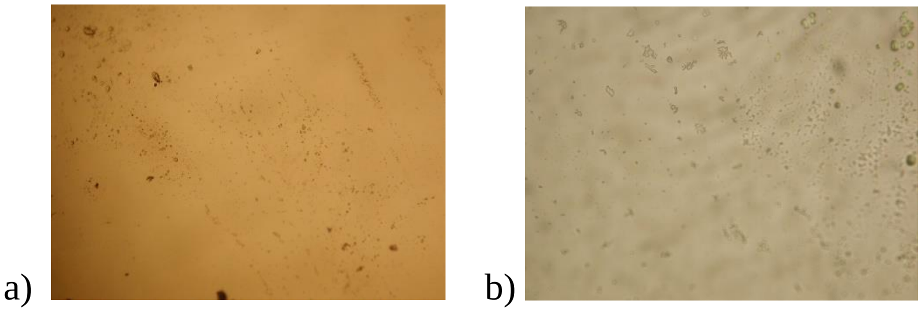
Type of skin	Clamping skin length at break, mm	Skin width, mm	Thickness, mm	Breaking load, kg/s	Strength of the skin kgs/ mm^2	Elongation, %
OMS-UFC	50	50	0,269	18,9	2,0	31
OMS-HYPAN	50	50	0,219	20,1	2,4	29
OMS-UFC- HYPAN	50	25	0,198	28,6	4,7	17

It can be seen from the data of the table that in the case of mechanical tests, the skin of the OMS-UFC-HYPAN composite, despite the much smaller thickness (and width) of the skins of OMS-UFC and OMS-HYPAN samples, shows rather high strength values, by 1.5-2 times . The relatively high strength of the composite skin is due to intermolecular interactions and the formation of chemical bonds between the components. In other words, in the internal morphological structure, there will be no large supramolecular formations characteristic of both natural formations and synthetic polymers.

It should also be noted that under the conditions chosen by us, the preliminary preparation of each component and the preparation of a thickening composite material from them, favorable prerequisites are created that ensure intensive interaction between the constituent components of the composite. Therefore, it is quite possible to form a homogeneous microstructure of a thickening composition capable of actively reacting, chemically bind to both cellulose chains and dye molecules.

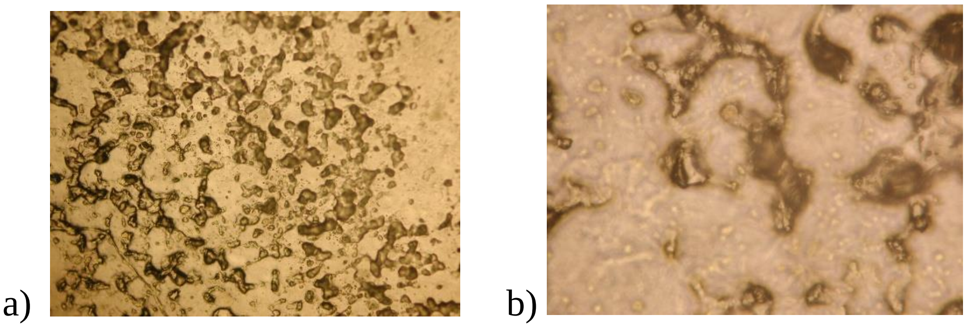
To verify the validity of the above conclusions, it seemed to us possible to conduct thorough microscopic studies of all the samples studied. To this end, we used a highly magnified optical microscope Nikon. Preparations for direct microscopic observations were prepared according to a known method [76]. Microscopic studies were carried out with the following samples: - modified starch (MS), i.e. Oxidized under certain conditions (as a control sample); - MS (6%) - HYPAN (0.08%); - MS (6%) - HYPAN (0.08%) - PAA (0.1%); - MS (6%) - HYPAN (0.08%) –PAA (0.1%) - Na_2SiO_3 (0.6%). Microscopic studies of the structure of thin skins of these samples were carried out at 40x, 100x and 400x magnifications. Picture 1-3 shows the main results of observations. In Pic. 1 a, b shows microscopic images of a thin skin of the initial oxidized-modified starch (OMS), respectively, 100 and 400 times magnifications. It can be seen that for a pure starch sample a relatively homogeneous microstructure is characteristic.

By its fine structure, starch is an amorphous substance (polysaccharide). Nevertheless, in the microstructure of its thin skin, especially at very high optical magnifications, it is possible to see some associates - aggregates of micro globular particles (Pic. 1b). When other components are incorporated into the starch, as expected, its microstructure changes dramatically.



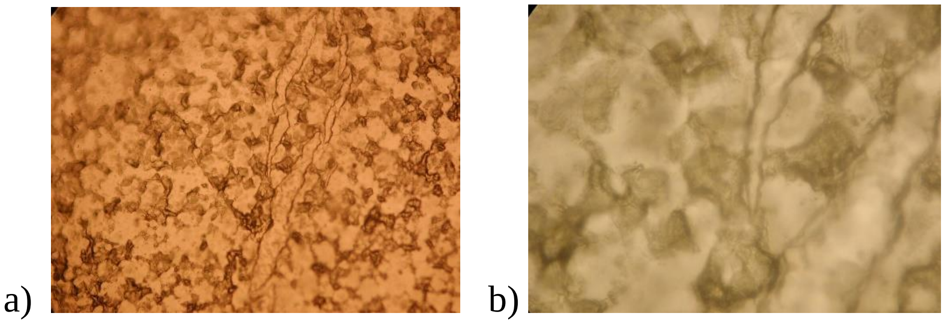
Pic.1. Micrographs of MS: a - 100^x magnified, b - 400^x magnified.

Thus, in Fig. Figures 2a and b show micrographs of skins of the OMS sample (6%) - UFC (0.08%) in the two above-mentioned direct optical magnifications. It is easy to see that even with a small amount of UFC (0.08%) in the total mass, the microstructure of the starch undergoes rather drastic changes. Throughout the mass, longer, more precisely an isodiametric particles are observed, which are supramolecular formations of UFC macromolecules. Their basis is composed of those macromolecules of the polymer, which did not have time to interact with the molecules of starch. In the same place, one should also point out the presence in the microstructure of the skin of OMS-UFC regions where there are no an isodiametric aggregates of UFC macromolecules (Pic. 2).



Pic.2. Micrographs of OMS - UFC: a - 100^x magnified, b - 400^x magnified.

Microscopic observations showed that with the appearance of the third component in the mass (OMS-UFC-HYPAN systems), the shapes and sizes of super molecular formations characteristic of UFC macromolecules strongly vary. From Pic. 3 a, 6 it is easy to see the inhomogeneous microstructure of the composition. At the same time, noticeable modifications of the microstructure, especially under the influence of the constituent components among themselves, can be seen from the presented microphotographs. This is particularly noticeable at large magnifications (Pic. 3b).



Pic.3. Micrographs of OMS – UFC - HYPAN: a - 100^x magnified, b - 400^x magnified.

From the data obtained and described above, it can be concluded that the HYPAN macromolecules, sufficiently reacting with the UFC macromolecules, modify both the chemical nature and their conformation. Obviously, this explains the destruction of the fine microstructure of previously observed an isodiametric UFC particles. Thus, important prerequisites are created for homogenizing the microstructure of the entire mass of the composite material.

It can be concluded that the results of microscopic studies confirmed the assumption that the newly developed thickening composition based on OMS, UFC and HYPAN will have, along with good physicochemical properties, also a very homogeneous (homogeneous) amorphous structure. The latter, though indirectly, indicates the possibility of a structural-chemical transformation of all the components included in the composite. Thus, the developed new composite printing thickener can be successfully used for packing cotton fabrics.

3.5. APPLICATION OF HARDENING COMPOSITIONS BASED ON OXIDIZED STARCH AT THE SCREEN OF TISSUE WITH ACTIVE DYES

The use of the proposed polymer system based on starch oxidized by us as a thickener is aimed at enhancing the coloring properties of the tissue and improving the fretboard when printing with active dyes. The composition of the developed and traditionally used thickeners is shown in Table 1. The rest of the components for the preparation of printing ink were carried out according to a known method [90].

Table 1

Compositions of thickeners for packing cotton fabrics

The proposed thickener, g/kg	Applied bunches in production, g/kg	
Oxidized starch -60	Sodium alginate -25	Starch – 90
Unifloc 0,29-1,6	Bicarbonate of soda -10	Sodium silicate – 3
HYPAN -1,0-1,6	Urea -100	Ludigol -10
PAA -0,3-0,6	Water -until 1 kg	Water -until 1 kg
Sodium silicate - 1		
Urea -100		
Ludigol -10		
Water -until 1 kg		

Fabric packing was carried out according to the technological regime of the textile enterprise, in which the developed thickener was tested. The results of the production tests are shown in Table 2.

Table 2

Qualitative characteristics of printed fabrics with active dyes

Thickener, dye	Lightness L (concentration of dye 40 g/kg)	Washability of thickener,%	Softness index,%
Imported thickener based on sodium alginate - SMT ("SNT", Berlin)			

Active Red 6C	43,4	97	96
Remazol Marine P-36	42,8	94	95
Remazol turquoise G	42,5	91	93
Composite thickener based on oxidized starch			
Active Red 6C	39,7	87	90
Remazol Marine P-36	38,6	83	85
Remazol turquoise G	40,1	86	88

The main end results of printing textiles are the intensity and strength of the stains. Printing was carried out under laboratory conditions of production by active dyes according to the approved technological printing conditions for this class of dyes. The results are shown in Table 3.

Estimating colors by intensity and strength parameters, it can be concluded that the three-component thickening composition OS-unifloc-HYPAN provides the required quality.

The thickening composition based on OS, HYPAN and Unifloc can be effectively used in the practical printing of textile materials with active dyes in order to improve the printing-technical properties of paints when used as a thickener.

Table 3

Final results of packing by three-component thickening compositions

Dye	Color indexes	OS/unifloc, mass fraction (C (HYPAN) = 1.24 mass%)					
		6/0,29	6/0,55	6/0,78	6/1,10	6/1,35	6/1,6
Active red 6C	Intensity K/S, unit.	13,52	13,52	13,21	13,36	13,48	13,76
	Stability to wash number 1, points	4-5/3-4	4-5/4	4/4	4/4	5/4	5/4
Active green 5J	Intensity K/S, unit.	9,54	9,65	9,65	9,74	9,82	9,91
	Stability to wash number 1, points	5/4	5/4	5/4	5/4	5/4	5/4
Active orange JT	Intensity K/S, unit.	12,03	12,06	11,95	11,95	12,16	12,23
	Stability to wash number 1, points	4/4	5/4	5/4	5/4	5/4	5/4

Thus, taking into account the compatibility of the blend components, it can be effectively used in the practical printing of textile materials, with the widest range of mass fractions of OS and unifloc. Approvable three-component thickening compositions have a complex of properties that predict the possibility of their effective use in printing textiles.

CONCLUSIONS

1. The main regularities of the process of starch modification with hydrolyzed polyacrylonitrile have been studied, the influence of temperature, concentration of alkali and polymer on the viscosity of polymer-polymer system solution has been revealed. It was found that the less pronounced viscosity anomaly of the starch-based composition and the carbo component polymer of hydrolyzed polyacrylonitrile is due to a weaker intermolecular interaction.

2. Changes in the viscosity of aqueous solutions have been studied for different ratios of natural and synthetic polymer compositions, in particular hydrolyzed polyacrylonitrile, unifloc and oxy-starch, it has been established that the viscosity of the solution of the composition is significantly influenced by the concentrations of the components. Moreover, an increase in the concentration of hydrolyzed polyacrylonitrile in the composition of the composition increases the viscosity of the aqueous solution of the latter.

4. The developed composition of the polymer composition possessed good thixotropic, i.e. the aggregates of the molecule of the composition that formed it were easily destroyed under the influence of mechanical influences, and after the cessation of the mechanical action it was restored again, this favorably affects the consistency of the printing ink during operation so that it does not change.

5. The advantages of the proposed composition of the composition allowing to completely replace the imported, expensive sodium alginate, empt or manitex are noted. It is found that the composition of the composition developed contributes to improving the printing, technical and rheological properties of the thickener for active dyes. In particular, increasing the viscosity of the coloring paste, which facilitates subsequent washing of the thickener from the fabric. It was found out that when using the composition as a thickener, the strength characteristics of the fabric after printing are increased.

BIBLIOGRAPHY

1. Takeda Yasuhito, Maruta Nohisa, Juliano Bienvenido O. Molecular structures of rice starch. “Carbohydr. Res.”, 1989, №189, p. 227-235.
2. Nagai Tadashi, Nademoto Yayoi, Yano Noshimasa. Improvement of physical properties by increase of specific surface area of starch gel powder. “J. Jap. Soc. Food Sci. and Technol.”, 1991, 38, №6, p. 533-539.
3. Larson Karl. Structure of the starch granule-A curves crystal. “Acta Chem. Scand.”, 1991, 45, №8, p. 840-843.
4. J. Whistler. Starch Chemistry and Technology. New York. Academic Press; 1984.
5. Vasanthan T, Hoover R. Comparative study of the composition of lipids association with starch granules from various botanical sources. Food Chem. 1992, **43,** p.19-29.
6. A.H. Clark, S.B. Ross-Murphy. Structural and mechanical properties of biopolymer gels. Adv. Polym. Sci., 1987, **83**, 55-192
7. Wiesenborn Dennis P. Behavior of paste potato starch connected from it by some natural and chemical properties. “J. Food Sci.”, 1994, 59, №3.
8. Технология крахмала и крахмалопродуктов. / Под ред.Н.Н.Трегубова. - М.: Лег.Пром. 1981, -472с.
9. Shefer A., Shefer S., Kost J., Langer R. Structural characterization of starch networks in the solid state by cross-polarization magic-angle-spinning ^{13}C NMR spectroscopy and Wide angle X – ray diffraction. Macromolecules, 1992, 25, № 25, p. 5756-6760.
10. Рихтер М., Аугустат З., Ширбаум Ф. Избранные методы исследования крахмала. М.: «Пищевая пром.», 1975, с. 105-140.
11. Wulff G., Kubic S. Helical amilose complexes with organic complexands. Microcalorimetrik and circular dichroitic investigations. «Macromol. Chem.», 1992, 193, №5, p. 1071-1080.
12. Lourdin, D.; Della Valle, G. and Collona, P. Influence of amylose content on starch skins and foams. *Carbohydrate Polymers*, 1995, **27**, p.261-270.

13. Zobel H.F. Molecules to granules: a comprehensive starch review. “Starch”, 1988, 40, №2, p. 44-50.
14. Altwell W.A., Milliken G.A. A note on determining, amilopektin A to B chain ratios. “Starch”, 1980, 32, №11 p. 362-364.
15. Thorn Werner, Mohazzeb Sharbanou Molecular weights, lengths and distribution of side-chains in α-D-polyclucanes. “Starch”, 1990, 42, №10, p. 373-376.
16. Hatanaka, Y.; Inaoka, K.; Ozboy, O.; Demiate, I.M.; Kobayashi, O.; Higashihara, M.; Hyiama, K. Study of some properties of starch isolated from halotolerant microalgae *Dunaliella*. *J. Appl. Glycosci.*, 1997, **44**, 515-522.
17. Buléon, A.; Colonna, P.; Planchot, V. and Ball, S. Starch granules: structure and biosynthesis. *International Journal of Biological Macromolecules*, 1998, **23**, 85-112.
18. V. J. Morris. Probing starch granule structure, functionality and breakdown using atomic force microscopy. Starch -2004. Inter. conf. UK. 2004. p. 24.
19. Boruch, M. Transformations of potato starch during oxidation with hypochlorite. *Starch/Starke*, 1985, **37**, 91-98.
20. Oates CG Towards an understanding of starch granule structure and hydrolysis. Trend Food Sci. Technol., 1997, **8**, 375–382.
21. Mali, S.; Grossmann, M. V. E.; Garcia, M. A; Martino, M. N. and Zaritzky, N. E. Microstrucural characterization of yam starch skins. *Carbohydrate Polymers*, 2002, **50**, 379-386.
22. Larson Karl. Structure of the starch granule-A curves crystal. “Acta Chem. Scand.”, 1991, 45, №8, p. 840-843.
23. Швир И., Лехерт Г. Рентгенографические и ядерные резонансные исследования структуры крахмала “Starke”, 1989, №1, p. 34-36.
24. Bader, H. G. and Göritz, D. Investigations on high amylose corn starch skins. Part I: Wide-angle X-ray scaterring (WAXS). *Starch/Stärke*, 1994, **46**, 229-232.
25. Б.Г.Ершов. Радиационно-химическая деструкция целлюлозы и других полисахаридов. Успехи химии, 1998, 67(4), с.353-375.

26. Gernat CH., Radosta S., Damaschum G., Schierbaum F. Determination of crystalline and phase analysis of starches from different sources. Proc. 4 th Int. Conf.: Phys. Properties Agr. Mater. And influence Technol. Process., Rostok, Sept. 4-8, 1989: 4 th ICPPAM. Vol. 1. Berlin, 1989, p. 219-223.
27. Oostergetel Gerrit T., Van Bruggen Ernst F.J. On the origin of low angle spacing in starch. “Starke”, 1989, 41, №9, p. 331-335.
28. H. Panda. The Complete Technology Book On Starch And Its Derivatives// New-Delhi.: Asia Pacific Business Press Inc. 2004.- 465 p.
29. Герман М.Л., Юрьев В.П. и др. Исследование механизма гелеобразования крахмала. «Применение магнитного резонанса в народном хоз-ве». Тез. Докл. Всес. Конф. Казань, 22-24 июня, 1988, ч. 3. с.38.
30. Y. Yao, X.Ding. Retrogradation of rice starch systems studied by pulsed NMR. AACC Annual Meeting. Charlotte, North Caroline, 2001.
31. Reuther F., Gernat Ch., Plietz P., Damaschum G., Schierbaum F. Structure in degraded starch polysaccharide-water system as revealed by X-ray scattering. “Macro’87: 31 IUPAC Macromol. Symp., Merseburg, June 30 th –Jule 4 th, 1987 Abstr. Pap. Microsymp. 2, Microsymp. 3” s.1, s. a. 227.
32. C.G. Biliaderis, J. Zawistowski. Viscoelastic Behavior of Aging Starch Gels: Effects of Concentration, Temperature, and Starch Hydrolysates on Network Properties; Cereal Chem., 1990, 67, 240-246.
33. I.M.Demiate, M.Oetterer, G.Wosiacki. Characterization of Chestnut (castanea sativa, Mill) Starch for industrial utilization. Int. Jour. Braz.Arch.of Biology and technology. 2001, v.44, №1, pp. 69-78.
34. Schierbaum F., Kettlitz B., Radosta S., Reuther F. Structure – properties relations as a basic concept for starch functionality. “Macro’87: 31 IUPAC Macromol. Symp., Merseburg, June 30 th –Jule 4 th, 1987 Abstr. Pap. Microsymp. 2, Microsymp. 3” s.1, s. a. 223.
35. German M.L., Blumenfeld A.L. and ad. Structure formation in systems containing amylase, amylopectin and their mixtures. “Carbohydr. Polym.”, 1992, 18, №1, p. 27-34.

36. Takeda Yasuhito, Maruta Nohisa, Juliano Bienvenido O. Mecular structures of rice starch. “Carbohydr. Res.”, 1989, №189, p. 227-235.
37. Weber H., Ströhle J. Современное состояние технологий предварительной и последующей обработок тканей.// Текс.пром., 1997. №3. С.7-9.
38. Жушман А.И. Производство модифицированного крахмала.//Пищ.пром. 1993. №9. С.11.
39. BeMiller, J. N. Starch modification: challenges and prospects. Starch/Starke. 1997, 49(4), 127-131.
40. Nebesny E., Shalski J., Scrozinsski A. Molekulare struktur und physikalischemische eigenschaften von löslishen starken und dextrinen.// Starke. 1989. 41. №8. p..289-293.
41. Непрерывный способ струйной варки и сушки распылением и крахмал с высоким амилозы, полученный этим способом. Патент №5131953. США. 1992.
42. Лукьнов А. Б., Зубрев Н. М. Совершенствование технологии окисленного желирующего крахмала.// Сах. пром. 1980. №3. С.44-45.
43. Bergh N.O. Starches, In Surface Application of Paper Chemicals. Blackie Academic and Professional, 1998, 1, pp. 69–108.
44. F.F.Takizawa, G.O.Silva, F.E.Konkel, I.M.Demiate. Characterization of tropical starches with potassium permanganate and lactic acid. Int. Jour. Braz.Arch.of Biology and technology. 2004, v.47, №6, pp. 921-931.
45. Деудин В. И., Видутис И.Г., Захаренко А. И. Вискозиметрическое изучение процесса окисления крахмала перекисью водорода.// Сах. пром. 1981. №4. С. 84-87.
46. Казарян Н. З. и др. Применение природных сополимеров в качестве загустителей в печати активными красителями.//Химия и техн. крашения. синтеза красителей и полим. матер. Иваново. 1981. С.84-87.
47. Способ повышения текучести клейстера крахмала с помощью перекиси водорода. Патент №3975206. США. заявл. 18.11.74. опубл. 17.08.76.

48. Parovuori, P.; Hamunen, A.; Forssell, P.; Autio, K. and Poutanen, K. Oxidation of potato starch by hydrogen peroxide. *Starch/Starke*, 1995, **47**, 19-23.
49. Chung, M. G.; Jeon, Y. S.; Lee, S. K.; Park, J. M. and Lim, B. S. Physicochemical properties of oxidized waxy maize starches with sodium hypochlorite. *Korean Journal Food Science Technology*, 1999, **30**, 42-48.
50. И.Скибида, А.Сахаров, Кто первым внедрит «Амидокс»? The Chemical Journal. Октябрь–ноябрь 2005. с. 57-59.
51. Kuakpetoon, D. and Wang, Y. J. Characterization of Different Starches Oxidized by Hypochlorite. *Starch/ Starke*, 2001, **53**, 211-218.
52. Hebeish, A., El-Thalouth, I.A., Refai, R. and Ragheb, A. Synthesis and characterization of hypochlorite oxidized starches. *Starch/ Starke*, 1989, **41**, 293-298.
53. S. Pietrzyk. The changes in the internal structure of starch granules caused by oxidation. Electron J. of Polish Agricult. Univ. Food Sci. and Technology, Vol. 8, Iss. 2. http://www.ejpau.media.pl/volume8/issue2/art-23.html.
54. Abd El-Thalouth I., Refai R., Ragheb A., Hebeish A. Свойства окисленного крахмала и цианэтилированного крахмала.// Starke. 1990. 42. №1. P.18-23.
55. Lipponen, J., Gron, J., Bruun, S-E and Laine, T.: Surface Sizing with Starch Solutions at High Solids Contents. Proc. TAPPI Metered Size Press Forum, TAPPI Press, Atlanta, GA, USA, 2002, pp. 129
56. Hung Ph. V., Morita N.. Effects of Granule Sizes on Physicochemical Properties of Cross-linked and Acetylated Wheat Starches // Starch/Starke. 2005. 57. p.413–420
57. El-Hinnawy S. I., Fahmy A., El-Saied H. M., El-Shirbeeny A. F., El-Sahy K. M.. Preparation and Evaluation of Hydroxyethyl Starch // Starch – Starke. 1982, 34, p. 65-68.
58. Ragheb A. A., El-Sayiad H. S., Hebeish A. Preparation and Characterization of Carboxymethyl Starch (CMS) Products and Their Utilization in Textile Printing// Starch – Starke. 1997, 49, p.238-245.

59. Милованов А.Д., Прусов А.Н. Влияние красителей и ТВВ на реологические свойства и структурные характеристики некоторых загустителей.// Текстильная химия, 2(7) 1995. С.59-61.
60. Wang J., Ramaswamy G. N., Gatewood B.M., Eom T. Kenaf, Flax, Wheat Straw and Cotton Fibers: Response to Reactive Dyes // Proceedings of the American Kenaf Society, San Antonio, TX, 1998, pp.154-158.
61. Якимчук Р.П., Мищенко А.В., Булушева Н.Е. Применение кубовых красителей (физико-химические основы) – М.: Легпромбытиздат, 1985. 192с.
62. Swinkels J.M. 1996, Industrial Starch Chemistry: Properties, Modification and Application of Starches, AVEBE, Foxhol, Netherlands. www.avebe.com.
63. Отделка изделий из химических волокон./Г.С.Сарибеков, Ю.И.Осик, Ф.В.Андросов, Л.И.Глущенка и др.// -К.:Техніка, 1982. -199с.
64. Предприятие Вимал производитель крахмалодуктов. www.vimal.h1.ru
65. Дымникова Н.С., Баранов А.В., Морыганов А.П. Особенности активирущего действия неорганической соли в прцессе термической фиксации дисперсных красителей с использованием мочевины.//Текстильная химия. 1998, №1(13), С.13-15.
66. Модифицированная крахмальная загустка для печати активными красителями. Гос.проект РФ. №10-007-99.
67. Иванов В.В., Кокшаров С.А., Мельников Б.Н. Влияние магнитного поля на протекание хинон-гидрохиноновых переходов кубовых красителей.// Текстильная химия. 1992. №2. –С.42-48.
68. Bayazeed A., Higazy A., Hebeish A. Synthesis and Applications of Reactive Carbohydrates Part I: Behaviour of Carboxymethyl Starch Before and After Acid Hydrolysis Toward Grafting with Acrylamide // Starch–Starke. 1987, Vol. 39, p. 288-291
69. Ибрагимова Ф.Б. Разработка исследование фосфорсодержащих полимерных композиций на основе дихлоргидрин глицерина с

полифосфатными соединениями и их применение. Диссертация канд. техн. наук. Ташкент, 2002,- 214с.

70. Ихтиярова Г.А. Разработка и исследование композиционных полимерных загустителей для печатания хлопчатобумажных тканей. Диссертация канд. техн. наук. Ташкент, 2004,- 124с.

71. Reagents. Chemical diagnosics. Merck KGaA. Darmstadt. Germany, 1996. 1344 p.

72. Лидин Р.А., Молочко В.А., Андреева Л.Л. Химические свойства неорганических веществ. / под ред. Лидина Р.А. -М.: Химия, 2000. -480с.

73. Кухарский М., Линдерман Я., Мальчевская Я., Рабек Т., Лабораторные работы по химии и технологии полимерных материалов / Пер. с поль. Л.Н.Седова и Л.К. Филиппенко - М.: Химия, 1965. -394с.

74. Лабораторные работы и задачи по коллоидной химии / Под ред. Ю.Г.Фролова и А.С.Гродского. – М.: «Химия», 1986. – 216с.

75. Кукин Г.Н., Соловьёв А.Н. и др. Лабораторные работы по текстильному материаловедению. М.: Легкая промышленность, 1974. –С.145-147.

76. Х.У.Усманов, К.Х.Розиков. Световая и электронная микроскопия структурных превращений хлопка. -Т.: Фан. 1974. 300с.

77. Браун Д., Флойд А., Сейнзбери М. Спектроскопия органических веществ: Пер. с англ. М.:Мир, 1992. — 300с..

78. М.С.Шарипов, М.М.Амонова, Х.Р.Адизова, Ш.Ш.Шадиева.Изучение изменения физико-химических и реологических свойств крахмала при модификации хлоратом натрия// Новый университет. -Москва, 2014. -№12. -С.84-89.

79. А.Н.Прусов, О.В.Алексеева, О.В.Рожкова и др. Реологические модификаторы - регуляторы физико-химических и физико-механических свойств водно-дисперсных систем// Текстильная химия, 1995, №2(7), С. 15-19.

80. Р.Г.Жбанков. Инфракрасные спектры целлюлозы и ее производных. Минск. «Наука и техника», 1964

81. Delwiche S.R., Pitt R.E., Norris K.H. Examination of starch-water and cellulose-water interactions with near-infrared (NIR) diffuse reflectance spectroscopy. *Starch.* 1991;43:415-422.
82. Р.Г.Жбанков. Инфракрасные спектры и структура углеводов. Минск «Наука и техника», 1972. –С. 78-118.
83. Некрасова В.В. Разработка новых загущающих систем на основе эфиров целлюлозы и крахмала для текстильной печати. Автореф. канд. техн. наук. – Иваново., 2010. – 15 с.
84. Ragheb A.A., El-Sayiad H.S., Hebeish A. Preparation and characterization of carboxymethyl starch (CMS) products and their utilization in textile printing. Starch/Starke, 1997, 49, 238–245.
85. Мельников Б. Н. Роль текстильных вспомогательных веществ. Прогресс текстильной химии и технологии // Рос.хим.ж. (Ж. Рос. хим. об-ва им. Д.И. Менделеева), 2002, т.XLVI, № 1 С.9-19.
86. М.Р.Амонов. Водорастворимые полимерные композиции на основе местного сырья для применении в производстве хлопчатобумажных тканей и технология их получения: Дисс…д-ра.техн.наук. –Ташкент, 2005. - 252 с.
87. Шарипов М.С., Мардонов С.Э., Ниёзов Э.Д., Асқаров М.А. Изучение особенностей реологических свойств гелей композиций на основе электрохимический модифицированного крахмала // ДАН РУз. – 2012. - № 1.- С. 63-66.
88. Кричевский Г.Е. Химическая технология текстильных материалов. – М., 2001. - Т.1: РЗИТЛ. - 480 с.
89. Шарипов М.С. Разработка технологии получения высокоэффективных загустителей на основе окисленного крахмала и водорастворимых полиакрилатов. Дис. канд. наук. Ташкент, 2008. -С.135.
90. Степанов А.С. Загустители печатных красок. –М.: Легкая индустрия. 1969, 174 с.
91. Белокурова О.А., Щеглова Т.Л. Перспективные технологии, материалы и оборудование для текстильной печати. –Иваново: ИвГХТУ, 2008. – 72с.

92. Шарипов М.С. Разработка новых композиционных загустителей на основе окисленного крахмала и водорастворимых полимеров для набивки хлопчатобумажных тканей//Химия и химическая технология.-Т.№4, 2015. – С.52-56.

Diploma work publications

1. Шадиева Ш., Шарипов М.С.,Аминова Ш. Олимов Б.Б. Выбор эффективного модификатора крахмала в целях получении его окисленного производного. Мат. респ. конф. Актуальные проблемы химической технологии. Бухара, 2014г. –С.77.
2. М.С.Шарипов, Э.Д.Ниёзов, Б.Б.Олимов. Изучение структурные изменения в процессе окисления рисового крахмала хлоратом натрия. Мат.научной конференции «Актуальные проблемы химии природных соединений»,Ташкент, 12 марта 2015г., - С. 236.
3. Шадиева Ш., Шарипов М.С.,Олимов Б.Б. Разработка новых композиционных загустителей на основе окисленного крахмала и водорастворимых полимеров. Научный вестник БухГУ. –Бухара, 2015. -№1, - С. 31-34.
4. М.С.Шарипов, Ш.Ш.Шадиева, Б.Б.Олимов, С.Э.Мардонов. Применение загущающих композиций на основе окисленного крахмала при набивке тканей с активными красителями/ «Композицион ва нанокомпозицион материаллар ва улардан маҳсулотлар олишнинг прогрессив технологиялари» республика илмий-техникавий конференцияси материаллари, Тошкент, 2015 йил 28-29 апрель, -156-157 б.
5. М.С.Шарипов, Б.Б.Олимов. Изучение изменений макромолекулярных свойств рисового крахмала при его окислении хлоратом натрия. Алматы. Химический журнал Казахстана, №2, 2015 г. –С.215-219.
6. Олимов Б.Б., Шарипов М.С., Тиллаева Д., Аскаров М.А. Изучение окисленного крахмала и композиций на его основе методом ИК – спектроскопии/ Международная конференция “Актуальные проблемы отраслей химической технологии”, Бухара, 2015. –С.211-214.

7. Шарипов М.С., Олимов Б.Б., Зиёдуллаев Б.М. Разработка технологии получения и изучение свойств крахмала разных сортов риса. Москва, Ученый 21 века., 2016. №4 (1), -С.3-5
8. Олимов Б.Б., Шарипов М.С., Зиёдуллаев Б.М. Процесс образование надмолекулярных структур в загущающих композициях на основе окисленного крахмала и водорастворимых полиакрилатов. Техника ва технологияларни модернизациялаш шароитида иқтидорли ёшларнинг инновацион ғоялари ва ишланмалари республика илмий-амалий анжумани. Тошкент, 2016 й. – 196-199 бетлар.