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2
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Vol. 77, No. 2

CONTENTS

CNF and Household Paper

Introduction of Research Laboratories (149)

Research Report

Pulp and Paper Mills in Japan (101)

2023 February JAPAN TAPPI JOURNAL
Vol.77, No.2 Abstracts

Properties and Application Development of Phosphorylated Cellulose Nanofibers

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Recently, woody biomass is expected to be used in multiple ways as a carbon-neutral and renewable resource. Among them, cellulose nanofibers (CNFs) are attracting attention as a new nanomaterial derived from cellulose, one of the major components of trees. We have established a unique CNFs production method by introducing phosphate groups to the hydroxyl groups of some of the cellulose molecules in wood pulp and mechanically processing the resulting phosphorylated pulp. The obtained phosphorylated CNFs were completely nanosized (about 3 nm in width) with high yield, and its aqueous dispersion was highly transparent, highly viscous, and stable at pH 3-11. Analysis of the surface chemical structure revealed the presence of cross-linked phosphate group as well as monophosphate group, which are selectively introduced only at the C2 and C6 positions of the hydroxyl group of the cellulose molecule. The aqueous dispersion of phosphorylated CNFs can be dehydrated and dried to form transparent CNFs sheet with densely intertwined CNFs. This sheet has high transparency, strength, and thermal dimensional stability, and at the same time, it has paper-like flexibility. In order to promote the practical use of this technology, we are currently operating a demonstration plant for the production of phosphorylated CNFs aqueous dispersion and phosphorylated CNFs sheet. As the first stage of practical application, the aqueous dispersion of phosphorylated CNFs is used as a thickening agent for cosmetics and a leading agent for concrete pumping, and the sheet is used as a material for table tennis rackets. We will continue to take advantage of the features of phosphorylated CNFs to develop further applications.

Paper with antiviral performance
-An application of CNF technology -

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A continuous decrease in the demand for printing paper is inevitable due to the trend of electronification. On the other hand, a constant increase in the need for different types of paper, such as wrapping paper and transport materials, is expected because switching from plastic to paper is a trend. Paper is a sustainable natural resource made from wood that can fix CO2. Therefore, we believe that developing paper-based materials with various functions will significantly contribute to the world from the perspective of SDGs and GHG reduction.

The philosophy of the Nippon Paper Group is "Contributing to better living and cultural progress everywhere it does business." The slogan is "Constantly creating new value and contributing to better living and cultural progress, as a comprehensive biomass company shaping the future with trees." Under this philosophy and slogan, we have combined paper manufacturing technologies, our primary business, and "cellulose nanofiber," the ultimate ultra-fine material manufactured from wood. This approach led to the development of antiviral paper, one of the most required properties worldwide. This paper material exhibits high antiviral properties against influenza virus, feline calicivirus, as well as new coronavirus. It also shows antibacterial and deodorant effects. In November 2021, we obtained the industry's first SIAA certification of antiviral-processed products in the category of "paper, copper and other inorganic materials, by embedding." It has now begun to be adopted for items, such as business cards and envelopes, requiring familiar infection prevention because unspecified people may touch it. It would be great if we could prevent contact infections in people's lives and contribute to safety.

Efforts of the installation CNF for racing car

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Since 2018, we have provided CNF materials to SAMURAI SPEED, which participates in US races, and have evaluated them by mounting them on electric vehicles. We have expanded the mounting locations every year and promoting the mounting of new products. In 2022, CNF composite resin for door mirrors, CNF molded plate for body, CNF products have contributed to weight reduction by mounting a continuous molded plate. In addition, even when driving in a harsh environment, it was possible to drive without any problem in terms of durability, similar to a normal vehicle. The CNF molded plate used in the body of a race vehicle is a material made by compounding CNF and pulp fiber into a sheet, and has mechanical properties far superior to those of general plastic materials. Moreover, since it is composed only of CNF and pulp, it is an environmentally friendly material. The CNF composite resin used in the door mirror, ELLEX-R55, is a CNF composite resin having a cellulose concentration of 55%. Since the resin reinforcing effect can be obtained by compounding cellulose as a resin filler, a plastic reducing effect can be expected. Utilizing the characteristics of CNF such as plant origin, high strength, high elastic modulus, and recyclability, we will contribute to CO_2 reduction by reducing plastics and weight of vehicles, and we will expand the CNF business in the medium-term business plan after 2024.

Microporous membrane with cellulose nano-fibers for Li-ion battery

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It is widely said that the non-woven fabric has a large pore diameter and hard to be applied as a separator for lithium ion batteries. In this study, we actually made some battery cells using non-woven fabric and conducted a confirmation test on the occurrence of defects. A hand-made PET non-woven fabric and a cellulose non-woven fabric were used for the test as a Lithium ion battery separator. A commercially available polyolefin microporous membrane and a developed microporous membrane with cellulose nanofiber (FIBLIC) were evaluated for comparison. As a result, in the PET non-woven fabric, a decrease in discharge / charge efficiency, which is guessed to be poor electrical insulation property, was observed in the initial aging process. No problem occurred in the aging process for the cellulose non-woven fabric, but in the 0 ° C float test (Charging on Constant Voltage at 4.2V), voltage fluctuations that seemed to be a slight short circuit due to dendrite formation were observed. The developed microporous membrane with cellulose nanofiber did not show any problems as in the polyolefin microporous membrane.

Development and Application of Weather Resistant Wood-paint using Cellulose Nanofibers

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Development of the wood paint superior in weatherability was achieved using unmodified cellulose nanofiber (CNF) made from domestic cedar chips. We used soda-anthraquinone cooking to prepare the pulp, and enzymatic pretreatment was performed prior to mechanical treatment for nanosizing process. The CNF water suspension prepared by the integrated process showed high dispersibility and was suitable for water-based paints compared to other CNFs. The accelerated weathering test with the coated wood panel using the CNF-blended water-based paint revealed that the degree of discoloration was suppressed to less than 1/2 than in the case without CNF.

CNF dispersion evaluation by particle size distribution measurement using high resolution disc centrifugal sedimentation method

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It is important to evaluate dispersibility since CNF are generally miniaturized by mechanical treatment under wet conditions. The particle size distribution evaluation is one of them, and it is important for controlling the physical properties of CNF and making effective use of it.

There are various principles and method for particle size distribution measurement, and each of them has a particle size range, a particle concentration and a dispersion medium, which they are good at. It is necessary to use it properly according to the sample to be measured and the purpose. CNF often has various particles size at the same time in the defibration process. Therefore in order to measure CNF with different particle size at the same time, it is necessary to select a particle size measurement method with high resolution. The centrifugal sedimentation method particle size distribution measurement method is attracting attention as a method for directly observing particles without using a fitting algorithm.

We prepared a sample that was mechanically processed in six steps from 1 to 30 times, and confirmed the difference in distribution using a disc centrifugal type particle size distribution analyzer. It was confirmed that the CNF was defibrated and the median diameter became smaller as the number of treatments increased. It can be expected to be used for physical property control and effective utilization of CNF.

OnGuard VBX Advance Vibration Monitoring for Improved Yankee Coating Performance

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To provide improved process awareness, an advanced vibration monitoring system that includes proprietary software and analytical techniques has been developed. The utilization of this new monitoring system will be reviewed highlighting its capability to optimize overall Yankee cylinder operation. A case study will demonstrate the value of this new monitoring system, a system that includes remote monitoring and control capabilities. Specifically, it will address the correlation of vibration characteristics with Yankee coating performance and crepe blade chatter.

Latest paper machine clothing development for Tissue and Toilet Papers

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Tissue paper manufacturing cost and paper quality are main “key drivers” for the papermakers. With this reality it is imperative that suppliers of paper machine clothing must provide innovative solutions in order to reduce these paper manufacturing cost and attain high sheet quality.

Albany International has developed specific product solutions to high, medium, and low speed tissue machines and for different kind of forming and press technologies like Crescent former and a new machine concept NTT. This paper describes new technology of Paper Machine clothing of forming wire, press felt, and shoe press belt.

Felt Designs for a wide range of products, from toilet to over 40g towels

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In recent years, domestic paper manufacturers have continued to focus on the production of household paper. Among them, there has been a marked increase in the production of toilet paper and paper towels, i.e., medium- to high-basis-weight household paper products. New entrants into the household paper market are also continuing, and new types of paper machines are increasingly being installed in Japan. The domestic household paper market will continue to be a focus of attention in the future due to the aging of the population and the expected resurgence of inbound demand.

We have five large felt manufacturing bases around the world with global operations, and our Austrian mill, one of the largest in the world and established over 200 years ago, has the world's top share in the household paper market, especially in Europe.

The company is also aggressively expanding into the aforementioned medium- to high-basis-weight products and new machine-type fields.

In this issue, we will introduce the features of the felt design that has become the mainstream in this field.

A New Approach for Stable Operation of Yankee Coating on Tissue Machines
-Solutions with Chemical and Digital Tools-

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Creping remains the most important unit operation in the tissue making process, particularly for conventional light dry crepe machines. As such, tissue makers should always be on the alert for new ways to improve this process. In this paper we introduce both a new creping adhesive and a new digital tool, vibration monitoring, to the Japan market as opportunities for process and product improvement.

The new Yankee coating adhesive is designed to provide a unique set of coating properties. The "TULIP™" adhesive provides strong adhesion, soft film characteristics, good tolerance to moisture variation, excellent durability, and superior rewet qualities. These properties are demonstrated by lab studies and commercial case histories. The strong adhesion over a wide moisture range can be utilized to improve crepe structure (increased number of crepe structures per unit length) to positively influence softness or maintain softness at higher creping moisture levels for energy savings.

The new digital tool is called "Yankee Operations Intelligence" or YOI and helps tissue makers protect their Yankee dryers by alerting them to potentially damaging chatter events. Although asset protection is a focus for YOI, vibration monitoring also provides powerful insight to mechanical, operational, and chemical impacts to the health of the Yankee coating and creping process. Vibration monitoring can easily detect changes and provide guidance to operators to make adjustments if needed.

Application of Fiber Recovery Basket with screen for Tissue line

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The recent target of Stock Preparation System is to improve stock quality, to save energy and to save fiber loss. Also the importance of water saving is also getting higher as other target. This means that effluent treatment is also need to be improved to get better recycled water to reduce the usage of flesh water.

Typical effluent treatment has two steps as primary (with DAF: Dissolving Air Flotation) and secondary (with sedimentation). After water clarification, sludge comes out from the system. Sludge includes some short fibers which can be reused, and usually sludge is treated by landfilling finally. If short fibers are reused it would save the cost not only of fibers but also of landfill.

To recover the short fibers usually Disc Filter is applied, but a Disc Filter need big installation area and expensive cost of machine itself. Therefore it is not still applied for many customers yet, especially for the customers in small production.

To recover more short fibers at effluent treatment in relatively small flow ratio, smaller and easier machine is necessary. In this article, I introduce the latest fiber recovery technology with screen basket.

The latest technology of Double-Drum Winder and KAWANOE Pilot Converting Line.

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Kawanoe Zoki Co., Ltd. has been involved in paper manufacturing machinery for over 70 years since its founding in 1944 under the management philosophy of "Let's work together and prosper together" Paper manufacturing machines have five functions: paper making, paper winding, paper folding, paper slitting and cutting, and paper wrapping.

We design and manufacture all machines with 5 functions.

Among them, this time I would like to introduce high-speed and automation technology of the two-drum winder for tissue-paper,board and paper,non-woven.

Preparation and Functionalization of Cellulose Nanofibers/Polymer Composite Particles Using Various Kinds of Core Polymers.

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In the present study, we investigated the development of dry powders comprising polymer particles covered with cellulose nanofibers (CNFs). CNFs with uniform widths can prepared from wood cellulose by TEMPO (2,2,6,6-tetramethylpiperidine-1-oxyl)-mediated oxidation, which introduces carboxy groups onto the surface of the cellulose. Divinylbenzene (DVB) monomer droplets are stabilized by CNFs in an aqueous emulsion system, and it is possible to obtain poly-DVB (pDVB) microparticles that are densely covered with CNFs by polymerizing the DVB in such a system. Herein, we developed an approach to fabricating CNF-shelled composite microparticles with cores comprising various types of polymers, and investigated the properties of their carriers.

We found that it was easier to stabilize the monomer droplets in an emulsion if the CNFs were modified with quaternary ammonium (QA) cations. This strategy enabled us to produce CNF-shelled composite microparticles with various types of core polymers. Moreover, the mechanical properties of these composite particles were superior to those of polymer microparticles without a CNF shell.

The electronic interaction with the surface carboxy groups of the CNF shell endowed the composite particles with the pH-sensitive ability to adsorb/desorb various cationic molecules, such as antibacterial agents, metal ions, polymers, and fluorescent or redox dyes. Interestingly, when fluorescent dyes were adsorbed onto the composite particles, the emission wavelength was shorter than in the solid state,
which suggests that interaction with the carboxy groups dissociated on the surfaces of the particles prevented the aggregation of the fluorescent dye.

The functionalized cellulose nanofibers/polymer composite particles produced by the process have desirable mechanical and carrier properties, and are therefore potentially very useful for industrial applications and in the security field.