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IMPROVEMENT OF OIL AND GREASE RESISTANCE OF CELLULOSIC MATERIALS

Juraj Gigac, Monika Stankovská, Mária Fišerová
Pulp and Paper Research Institute
Bratislava, Slovak Republic

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ABSTRACT

The oil and grease resistance of paper after surface sizing with aqueous dispersions composed of film forming polymers, their mixtures with fluorinated polymer or fluorinated polymer and silver nanoparticles was compared. The oil and grease resistance of paper was regulated by changing the composition and intake of aqueous dispersions and paper grade, and it was evaluated by the content of fine surface pores, contact angle, oil absorptiveness, grease resistance, oil repellency on the inclined surface and oil penetration time. The aqueous dispersions were applied on one side and on both sides of paper surface in the size press. The film forming polymer has created a physical barrier against oil and grease, while combination with the fluorinated polymer developed a physical and chemical barrier. The papers sized with aqueous dispersions containing a mixture of film forming and fluorinated polymer with the addition of silver nanoparticles, achieved high oil and grease resistance even with lower consumption of the fluorinated polymer, and also achieved an antimicrobial surface. The more porous paper has achieved the required oil and grease resistance at higher polymers intake.

KEYWORDS: Packaging paper, surface pores, polyvinyl alcohol, fluorinated compounds, silver nanoparticles, oil and grease resistance

INTRODUCTION

The production of oil and grease resistant paper is based on minimizing the pores in the paper structure and closing the pores on the paper surface to prevent penetration of oil and grease from the surface into the paper structure. Oil and grease resistance is achieved by a high beating degree of pulp, but the result is increase of electricity consumption. At the same time, drainage rate is reduced, resulting in increased moisture and energy consumption during drying phase. This reduces the productivity of papermaking and increases the capacity requirements of the drying part of the paper machine. Papers made from pulp with a high beating degree contain pores of fine dimensions with a narrow range of pores size distribution.

Extrusion coating and lamination using molten polyolefins is one of the main techniques for creating a barrier against oil and grease. Oil and grease resistant papers prepared by laminating, extrusion or coating also have good barrier properties against oxygen permeability and to preserve the aroma of the packaged product. Polyethylene, polypropylene and the like extruded and laminated papers are not biodegradable and their recycling is difficult.

For the technical and economic reasons of oil and grease resistant paper production, the process of surface coating of various compositions is used. In various application techniques of film forming aqueous dispersion, the styrene-acrylate copolymers, polyvinyl alcohol or biodegradable polymers such as modified cellulose, starch, chitosan, pectin, polystyrene-butadiene or polyacrylate dispersions filled with inorganic pigment are used.

Fluorinated compounds represent a group of organic compounds in which a high percentage (up to 7%) of hydrogen atoms is replaced by fluorine atoms, resulting in the formation of a low surface energy molecule. Various functional groups may be present in the molecule of the fluorinated compound. Anionic, cationic, amphoteric or nonionic groups are generally bonded via a hydrocarbon group. Polymers and copolymers formed by polymerizing monomers with a functional group added to the chain of the fluorinated compound exhibit a wide range of properties such as hydrophobicity, hydrophilicity, oil and grease resistance, solution stability, pigment compatibility, heat resistance, pH stability and ionic compatibility.

Papers treated with fluorinated compounds have low surface energy and therefore there is a large contact angle between the paper surface and the oil drop. Strong adhesion forces increase the contact surface between the oil and the paper surface in all cases except paper treated with fluorochemicals. Phosphates and carboxylates of fluorinated compounds are used in the manufacture of paper and board packages to provide oil and grease resistance. They are easy applied to paper stock in a paper machine or on a paper surface in coating equipment. Since such treated materials are not physical barriers, they do not create a film, do not affect the porosity, the speed of water vapour permeability or the flexibility of the paper. Surface treated paper contains invisible chemical barriers that resist the penetration of oils and greases without affecting the porosity of the paper, as can be achieved by a high beating degree of pulp, extrusion and lamination with polyolefins, or when it is treated with aqueous dispersions of polymers forming surface film. Such papers are characterised by good fiberizing and recyclability. Phosphates and carboxylates of fluorinated compounds may be applied to the paper along with other ingredients such as alkyl ketene dimer, alkyl succinic anhydride, styrene maleic anhydride copolymer in order to increase its resistance to oil and water.

The fluorinated compounds can be incorporated as additives to the coating compositions of colloidal kaolin (Johnston et al. 2014) for obtaining oil resistance, which can differ depending on the type and the amount of additive, the composition and the weight of the coating and on the method of application. Fibres, fines, fillers and chemical additives affect fluorochemical coating by chemical or physical manner. Physical factors include the nature of the surface determined by the type of fibres, refining, kind and amount of fillers. Paper produced from bleached pulp is more easily treated than paper from unbleached pulp. Likewise, paper from softwood pulp is more easily treated than from hardwood pulp.

The major manufacturers of aqueous dispersions of fluorinated compounds for paper and board are company DuPont (USA) with products Capstone P-620 and P-640, AGC Chemicals (Japan) with products of the AsahiGuard E series as AG-E060, AG-070, AG -080 and Archroma (Switzerland) with Cartaguard series products. Capstone P-620 is a cationic fluorinated acrylate copolymer and Capstone P-640 is fluorinated anionic polyurethane. AG-060 and AG-E070 are slightly cationic fluorinated polymers, and AG-E080 is an anionic fluorinated polymer for application in size press. All product types are suitable for contact of papers and boards with food. Cartaguard KST liquid is a cationic fluorinated polymer containing perfluorooctanoic acid (PFOA) below the detection limit. According to BfR (Bundesinstitut für Risikobewertung) recommendation, Cartaguard KST liquid is suitable for food contact applications, with a maximum concentration of commercial product in paper and board of 22 mg dm^{-2}. Phosphates of fluorinated compounds are the most widely used additives for clay compositions with oil resistance. Fluorinated compounds based on telomere C8 require conversion to telomere C6 and perfluoropolyether (PFPE) of fluorinated compounds, for which less risk of degradation on products harmful to the environment is assumed. These fluorinated compounds are somewhat less effective in terms of oil resistance and the conversion process itself is costly and time-consuming (Johnston et al. 2014). Therefore, it is still necessary to improve the application methods and to find suitable compositions to achieve higher resistance of papers and paper products against oil in order to reduce the consumption of fluorinated compounds, negative environmental impacts and also costs.

Fluorinated compounds are used in pigmented coatings on the outside of boxes or bags to prevent contamination and maintaining the appearance of the package. Paper products resistant to oil and grease are most often used where a short contact time between grease substances and paper is, such as fast-food packaging papers. Oil and grease resistant papers are often used for longer-term storage of products such as butter and margarines.

The aim of this study was to improve the oil and grease resistance of the paper by surface sizing with aqueous dispersions with reduced content of fluorinated polymer.

MATERIAL AND METHODS

Material

Paper H - tesliner from recycled fibres, basis weight 127 g m^{-2} (Rondo Ganahl); paper E - testliner, two-layer from recycled fibres and unbleached pulp, basis weight 90 g m^{-2} (Hamburger).

Film forming polymer P - polyvinyl alcohol PVOH 28-99 with a dynamic viscosity of 4% solution of 28 mPa s and a degree of hydrolysis of 99%; film forming polymer PN - polyvinyl alcohol PVOH 10-98 with a dynamic viscosity of 4% solution of 10 mPa s and a degree of hydrolysis of 98%; fluorinated polymer F - anionic aqueous dispersion of fluorinated polyurethane phosphate.

Colloidal Silver S solution with an average particle size of 80 nm.

Commercial aqueous dispersion of polymers K1 - free of fluorinated compound, designed to create an oil and grease resistant barrier for paper and board; commercial aqueous dispersion of polymers K2 - free of fluorinated compound, designed to form an oil and grease resistant barrier for paper and board.

Castor oil, a surface energy of 34.5 mJ m^{-2} and a dynamic viscosity of 840 mPa s at 25°C.

A set of 12 solutions for determination of grease resistance (Kit test). The solutions contain castor oil, toluene and n-heptane, the relative ratios of these components and the surface energy of the solutions were reported in patent (Long et al. 2015).

The test oil (surface energy 26.8 mJ m^{-2}, dynamic viscosity 2.7 mPa s at 25°C) for an objective measurement (HST photometer) of penetration time contained 37 wt. % maize oil, 43 wt. % heptane, 20 wt. % 2-ethoxyethanol and 0.02 wt. % powder dye CI. No. 61565 Solvent Green (Liu 2005).

16% aqueous solution of isopropyl alcohol (IPA) with a surface energy of 44.2 mJ m^{-2} and a dynamic viscosity of 0.9 mPa s.

Methods

The content of fine surface pores

The fine surface pores content (T95) on the paper surface was determined by the ultrasonic device PDA-C.02 (Emtec, Radnor, PA, USA) as the penetration time of 16% aqueous solution of isopropyl alcohol for which the intensity of the ultrasound signal transferred to the paper dropped from 100 to 95%. The longer penetration time corresponds to the higher content of fine surface pores.

Contact angle of castor oil on paper surface

The contact angle of wetting the surface of the paper with castor oil was measured using optical tensiometer OCA 35 (Dataphysics Instruments, Germany) and recorded at the rate of 20 images per second in a time from 0.5 ms to 30 minutes. Contact angle values at 0.5 ms are marked as SCA_0, at 5 sec as DCA_5 and 30 minutes as DCA_{1800}.

Absorptiveness of castor oil

Absorptiveness of castor oil was determined by the Cobb method according to ISO 535. The absorptiveness values of castor oil $Cobb_{120}$ express the absorbed amount of oil per unit area of paper in g m^{-2} in 120 seconds.

Grease resistance (Kit test)

The grease resistance of paper and cardboard was determined according to ISO 16532-2. The Kit test consists of the application of solutions No. 1 to 12, wherein the solution No. 1 is the least aggressive, with the highest surface energy, viscosity and contact angle on the test paper surface, and solution No. 12 is the most aggressive, has the lowest surface energy (22.0 mJ m^{-2}), viscosity and contact angle. Solution No. 1 contains 100% castor oil. In solutions No. 2 to 10, the castor oil content is gradually reduced while the solvents content of n-heptane and toluene increased, their ratio in the mixture is 1/1. Solution No. 11 contains only solvents in a ratio of 1/1 and solution No. 12 also only solvents with a different ratio of 45% toluene and 55% n-heptane. Various Kit solutions fall on paper from a height of 4 cm and after 15 seconds they are quickly removed using fabric or tissue paper. The Kit value corresponds to the highest solution number, when the footprint still does not remain on the surface of paper or board.

Oil repellency on inclined surface

Oil repellency was determined by the modified Korean method KS M 7057, which determines water repellency of paper and board. The method is based (Kim et al. 2003) on falling drop of test liquid on a paper placed below 45° and evaluating the liquid footprint corresponding to each degree of repellency from the smallest R0 to the highest R10.

Oil penetration time

The oil penetration time is the time after which the penetrated oil footprints appear on the opposite side of the paper. The influence of surface sizing and base paper on the oil penetration time of two-sided sized papers was evaluated by a visual method with castor oil having a surface energy of 34.5 mJ m^{-2} and a dynamic viscosity of 840 mPa s at 25°C and by objective method using HST photometer (Hercules Sizing Tester). In the test, diluted maize oil containing green dye was used. Its surface energy was 26.8 mJ m^{-2} and a dynamic viscosity was 2.7 mPa s at 25°C. The HST photometer measures the time of reflectance decrease on the opposite side of the paper during solution penetration top side of paper. Simultaneously with the test solution pouring onto the paper surface, stop watch are started. After the reflectance drops from 100% to an adjusted 80% value, the stopwatch automatically switch off. Longer penetration times indicate a higher degree of oil repellency. The detailed procedure and possibilities of setting the measurement conditions with the HST photometer are described in the patent (Liu 2005).

Aqueous dispersions and surface sizing

For the surface sizing, 7 following aqueous dispersions were used:

- P, which contained 4 wt. % polyvinyl alcohol PVOH 28-99,
- PN, which contained 7 wt. % polyvinyl alcohol PVOH 10-98,
- P+F, which contained 7.2 wt. % of polymers mixture composed of 55% polyvinyl alcohol PVOH 28-99 and 45% fluorinated polyurethane phosphate,
- PN+F, which contained 10.2 wt. % of polymers mixture composed of 70% polyvinyl alcohol PVOH 10-98 and 30% fluorinated polyurethane phosphate,
- P+F+S, which contained 3.9 wt. % of polymers mixture composed of 55% polyvinyl alcohol PVOH 28-99, 45% fluorinated polyurethane phosphate and 200 ppm silver nanoparticles,
- Commercial aqueous dispersion of polymers K1 free of fluorinated compounds,
- Commercial aqueous dispersion of polymers K2 free of fluorinated compound.

The aqueous dispersions were applied one- and two-sided on surfaces of papers H and E in laboratory size press Werner Mathis AG at a constant paper speed (5 m min^{-1}) and pressure between rolls (980 kPa). Subsequently, the sized paper was dried on a photo dryer at 105°C for 3 minutes and sintered on each side at 140°C for 1 minute. The sized paper labelling comprises the type of the paper H or E, the top side T or the underside U of paper, number of passings through the size press 1 to 4, and finally the type of used aqueous dispersion (P, PN, P+F, PN+F, P+F+S, K1 and K2). For example, ET_2(PN+F) is the labelling of paper E with two passings through the size press using the aqueous dispersion composed of polymers mixture PN+F.

RESULTS AND DISCUSSION

Characterisation of base papers

For selection of methods to determine the effectiveness of sizing with aqueous dispersions, important properties which will be evaluated are choice of test liquid, conditions and limits of the tests with respect to the end use of the paper. The movement of the test liquid can take place over the surface (spreading and feathering) or the liquid can penetrate inside and through the paper sheet or the liquid can penetrate in and through the paper sheet.

The characteristic properties of H and E papers are shown in Tab. 1. The content of fine surface pores (T95) of paper H on top side T was 0.68 s and 5.43 s on underside U. The content of fine surface pores (T95) of paper E on top side was 0.20 s and 0.25 s on underside. Paper E is more porous compared to paper H because it contains less fine surface pores. This also corresponds to the absorptiveness of compared papers. The absorptiveness of castor oil Cobb$_{12}$0 of paper H on side was 48 g m^{-2} and 52 g m^{-2} on underside, representing 53% and 58% at basis weight of paper 90 g m^{-2}. The absorptiveness Cobb$_{120}$ of paper E on side was 84.2 g m^{-2} and 88.2 g m^{-2} on underside, which is 66% and 69% at basis weight of paper 127 g m^{-2}. The contact angle of castor oil SCA$_0$ on surface of paper H on top side was 80° and 74°on underside, in the fifth second, DCA$_5$ dropped to 51° and 46°, respectively, and in thirtieth minute DCA$_{1800}$ dropped to 30° and 23°, respectively. The contact angle of castor oil SCA$_0$ on surface of paper E on top side was 72° and 67° on underside, in the fifth second, DCA_5 dropped to 45° and 46°, and in thirtieth minute, DCA_{1800} dropped to 12° and 13°, respectively. Both papers had value of Kit 1, the castor oil feathered on the surface and immediately penetrated on the opposite side of paper.

Tab. 1: Characteristic properties of base papers H and E.

Paper and side	HT	HU	ET	EU
Content of fine surface pores T95 (s)	0.68	5.43	0.20	0.25
Absorptiveness of castor oil $Cobb_{120}$ (g m^{-2})	48.1	52.0	84.2	88.2
Contact angle of castor oil* SCA_0 (°)	80	74	72	67
Contact angle of castor oil * DCA_5 (°)	51	46	45	46
Contact angle of castor oil * DCA_{1800} (°)	30	23	12	13
Grease resistance (Kit test)	1	1	1	1

* surface energy of castor oil 35.0 mJ m^{-2}

In Fig. 1, images of oil footprint on the inclined surface of top side T and underside U of papers H and E after 1 hour of contact are shown. The oil footprints are wide because the oil feathered into the sides and penetrated on the opposite side of the paper immediately. The degree of oil repellency was the lowest, which corresponds to R0.

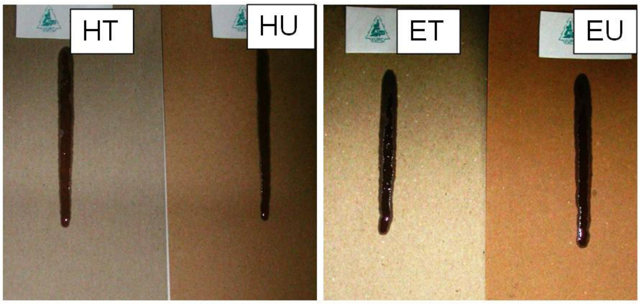

Fig. 1: Images of castor oil footprint on inclined surface of top side T and underside U of papers H and E after 1 hour of contact.

One-sided sized paper

Polyvinyl alcohol (PVOH) is a water-soluble polymer with applications for surface treatment of paper. It is the only biodegradable polyvinyl type of synthetic polymer. This polymer fills the pores in the paper and creates a film on a paper surface with high cohesive energy and good barrier properties against gases, which depend on humidity. With increasing humidity, the hydrogen bonds between polar groups of PVOH are disrupted, resulting in a deterioration of the barrier properties against gases. The average molecular weight of PVOH ranges from 13 to 124 kDa and the degree of hydrolysis from 80% to 99.9%. Modification of PVOH by organic compounds such as acrylates or carboxylic acid anhydrides can improve the barrier properties of PVOH coatings and allow their application in the food industry. Sized papers H and E on top side and underside were characterised by the content of fine surface pores, absorptiveness and contact angle of castor oil, and grease resistance (Kit test).

Fig. 2 shows the effect of surface sizing with aqueous dispersions of polyvinyl alcohols P and PN on the content of fine surface pores of sized papers H and E. The PVOH intake increased with the number of paper passings (1-4) in the size press. The underside of paper H had a high content of fine surface pores (T95) of 5.43 s, which increased to 14.2 s after four passings of paper through the size press. Paper E had a significantly lower content of fine surface pores than paper H. At 2.5 times higher PVOH intake, the content of fine surface pores (T95) was between 5.2 s and 5.4 s depending on the evaluated side of the sized paper E. Papers sized with PVOH had a higher content of fine surface pores than base papers, which indicates the formation of a physical barrier against liquids.

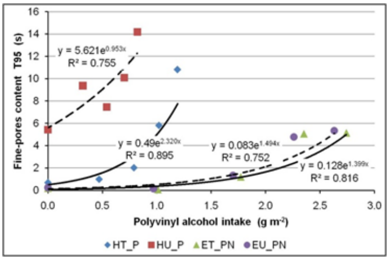

Fig. 2: Influence of surface sizing with aqueous dispersions of polyvinyl alcohols P and PN on the content of fine surface pores on top side T and underside U of papers H and E (after one to four passings through the size press).

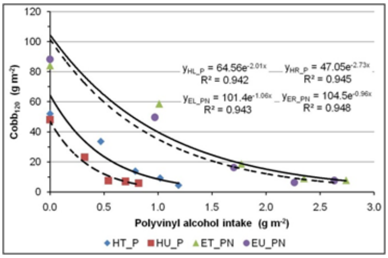

Fig. 3: Influence of surface sizing with aqueous dispersions of polyvinyl alcohols P and PN on absorptiveness of castor oil on top side T and underside U of papers H and E (after one to four passings through the size press).

Paper E is more porous than paper H because it contains less fine surface pores. This is the main reason that the absorptiveness of castor oil Cobb_{120} on the top side and underside of paper E was significantly higher compared to paper H at the same PVOH intake (Fig. 3). The sized paper E at intake of 1 g m^{-2} PVOH had absorptiveness of castor oil 40 g m^{-2}, while the sized paper H had only 5.5 g m^{-2}. Sized paper E had an absorptiveness of castor oil 7.7 g m^{-2} at intake of 2.7 g m^{-2} PVOH.

Paper H was more resistant (Kit test) compared to paper E (Fig. 4). PVOH intake required to achieve value Kit 5 was reduced in order of the sized papers: EU = ET > HT > HU, which is related to the increase of the fine surface pores content (Fig. 2).

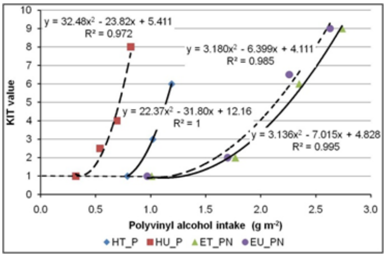

Fig. 4: Influence of surface sizing with aqueous dispersions of polyvinyl alcohols P and PN on grease resistance of top side T and underside U of papers H and E (after one to four passings through the size press).

A significant improvement in the efficiency of film forming polymers P and PN in terms of castor oil absorptiveness and grease resistance was achieved by adding fluorinated polymer F to aqueous dispersions. In Fig. 5, the effect of adding fluorinated polymer F to film forming polymer P on the properties of both sides of paper H with the higher content of fine surface pores is compared. The intake of polymers of 0.95 g m^{-2} on top side T with the mixture of polymers P+F was achieved with one passing through the size press while with the film forming polymer P itself with three passings (Fig. 5a). The absorptiveness of castor oil (Cobb$_{120}$) was approximately at the same level of 9.3 g m^{-2} and 9.7 g m^{-2}, respectively. Addition of fluorinated polymer F increased grease resistance from value Kit 3 to Kit 7 and the content of fine surface pores (T95) from 5.8 s to 7.6 s. The intake of polymers on underside U 0.95 g m^{-2} was achieved with the mixture of polymers P+F with two passing through the size press, while with the film forming polymer P alone, four passings were required (Fig. 5b). The absorptiveness of castor oil (Cobb$_{120}$) was 5.9 g m^{-2} and 6.1 g m^{-2}, respectively. Addition of fluorinated polymer F increased grease resistance from value Kit 8 to Kit 12. The content of fine surface pores (T95) after four passings with film forming polymer P increased to 14.2 s and with the mixture of polymers P+F after two passings, T95 reached only 7.7 s.

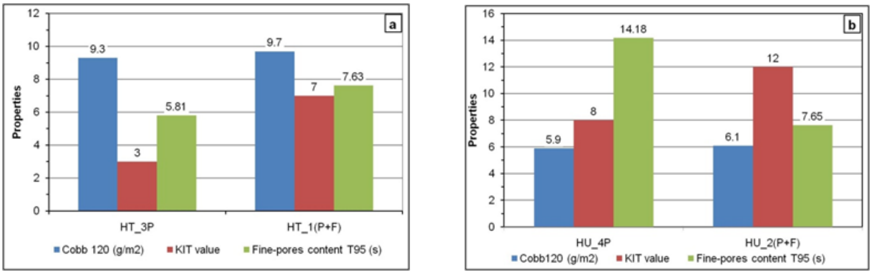

Fig. 5: Comparison of castor oil absorptiveness (Cobb$_{120}$), grease resistance (Kit) and content of fine surface pores (T95) of top side T (a) and underside U (b) of paper H after surface sizing with polyvinyl alcohol P, the mixture of 55% polyvinyl alcohol P and 45% fluorinated polymer F at intake 0.95 g m^{-2}.

In Fig. 6, the effect of fluorinated polymer F addition to film forming polymer P on the properties of both sides of paper E with the lower content of fine surface pores is shown. Intake of 1.7 g m^{-2} polymers on the sides T and U was achieved with the mixture of polymers PN + F with one passing through the size press, while with the PN polymer alone, it was achieved with two passings. On top side of paper E (Fig. 6a), the absorptiveness of castor oil (Cobb$_{120}$) was 18.6 g m^{-2} for the film forming polymer PN alone and 17.9 g m^{-2} in the case of the mixture of polymers PN+F. Addition of fluorinated polymer F increased grease resistance from value Kit 2 to Kit 6 and content of fine surface pores (T95) from 1.2 s to 5.4 s. Paper E sized on underside with film forming polymer PN (Fig. 6b) had absorptiveness of castor oil (Cobb$_{120}$) of 16.3 g m^{-2} and when sized with the mixture of polymers PN+F it was 15.3 g m^{-2}. Addition of fluorinated polymer F increased grease resistance from value Kit 2 to Kit 6, similarly as on top side. The content of fine surface pores (T95) after sizing with film forming polymer PN was 1.4 s and with the mixture of polymers PN+F was 8.6 s.

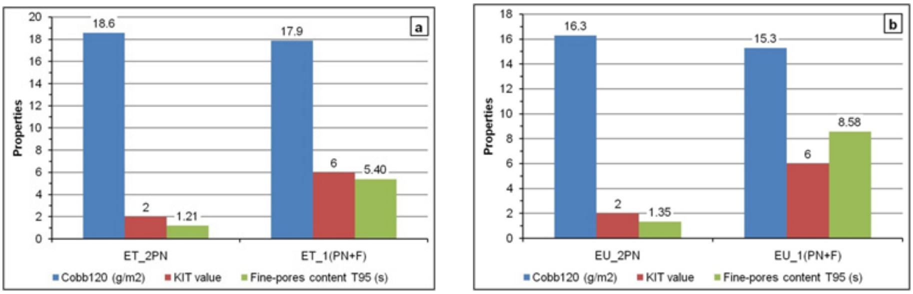

Fig. 6: Comparison of castor oil absorptiveness (Cobb$_{120}$), grease resistance (Kit) and content of fine surface pores (T95) of top side T (a) and underside U (b) of paper E after surface sizing with polyvinyl alcohol PN, the mixture of 70% polyvinyl alcohol PN and 30% fluorinated polymer F at intake 1.7 g m^{-2}.

The effect of fluorinated polymer F addition to the film forming polymer P on the properties of both sides of paper E is compared in Fig. 7. The intake of polymers on sides T and U of 2.8 g m^{-2} was achieved with the mixture of polymers PN+F with two passings through the size press, while with the film forming polymer PN alone with four passings. On top side of paper E (Fig. 7a), the absorptiveness of castor oil (Cobb$_{120}$) was 7.7 g m^{-2} for the film forming polymer PN alone and for the mixture of polymers PN+F of 5.5 g m^{-2}. Addition of fluorinated polymer F increased grease resistance from value Kit 9 to Kit 12 and the content of fine surface pores (T95) increased from 5.2 s to 5.8 s. On underside of paper E (Fig. 7b), in the case of the film forming polymer PN alone, the absorptiveness of castor oil (Cobb120) was 7.7 g m^{-2} and when used the mixture of polymers PN+F it was 6.6 g m^{-2}. Addition of fluorinated polymer F increased grease resistance from value Kit 9 to Kit 12, similarly as on top side. The content of fine surface pores (T95) after sizing with the film forming polymer PN was 5.4 s and with the mixture of polymers PN+F was 6.1 s.

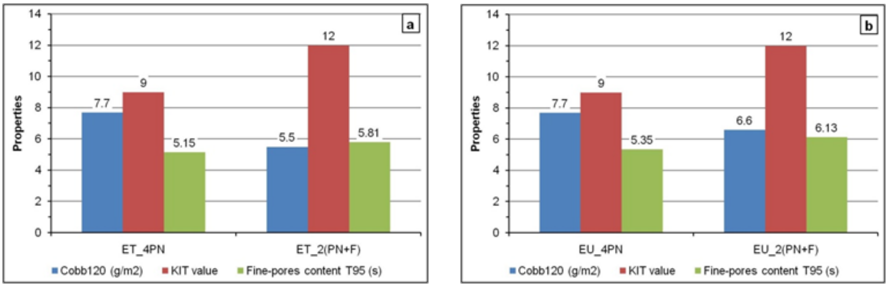

Fig. 7: Comparison of castor oil absorptiveness (Cobb$_{120}$), grease resistance (Kit) and content of fine surface pores (T95) of top side T (a) and underside U (b) of paper E after surface sizing with polyvinyl alcohol PN, the mixture of 70% polyvinyl alcohol PN and 30% fluorinated polymer F at intake 2.8 g m^{-2}.

Silver nanoparticles with a particle size of 10-60 nm have antimicrobial properties. They are mainly used for disinfection of drinking water and hospital premises. The antimicrobial effects of silver nanoparticles were studied in the surface treatment of packaging paper in combinations with cellulose nanofibres (Amini and Azadfallah 2016), chitosan (Nechita 2017) and curcumin (Arulmoorthy and Srinivasan 2015, Loo et al. 2016). Addition of silver nanoparticles to aqueous dispersions composed of a mixture of film forming and fluorinated polymers exhibited besides antimicrobial effects also a beneficial effect on the resistance of paper and board against the oil and grease, which is the subject of patent application (Gigac et al. 2018).

In Fig. 8, the effect of silver nanoparticles addition S to the mixture of polymers P+F on the properties of paper H on top side T is presented. After surface sizing with the aqueous dispersion of polymers with the silver nanoparticles addition P+F+S with a lower intake (5%) as in the case of mixture of the polymers P+F without silver nanoparticles, the castor oil absorptiveness decreased from 9.7 to 7.3 g m^{-2} (by 25%), the grease resistance increased from value Kit 7 to Kit 8.5 while the content of fine surface pores T95 decreased from 7.6 s to 7.0 s. It follows that the addition of silver nanoparticles to the aqueous dispersions of the mixture of polyvinyl alcohol and fluorinated polymer allows reducing their consumption while improving the resistance of paper against oils and grease. The addition of silver nanoparticles is advantageous to use to reduce the content of the fluorinated polymer in the aqueous dispersion, which has a positive effect on the environment.

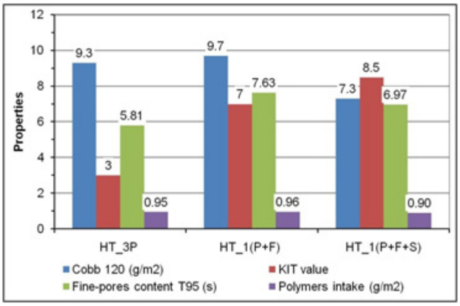

Fig. 8: Comparison of castor oil absorptiveness (Cobb$_{120}$), grease resistance (Kit) and content of fine surface pores (T95) of top side T of paper H after surface sizing with polyvinyl alcohol P, the mixture of 55% polyvinyl alcohol P and 45% fluorinated polymer F without and with the addition of 200 ppm silver nanoparticles S.

In Fig. 9, images of castor oil footprints on inclined surface of sized paper E on top side T and underside U after 1 hour of contact are shown. The oil footprints in Figs. 9a-d are wide, but the oil repellencies on the inclined surfaces were higher (degree of repellency R2-R4) compared to the base papers in Fig. 1 (R0). Oil footprint on paper with intake of polymers mixture P+F of 0.6-1.0 g m^{-2} (Fig. 9e) was significantly narrower (R7). In Figs. 9f,g oil footprints were interrupted (R9-10) as papers sized with the mixture of polymers P+F (intake of 1.1-1.8 g m^{-2}) and the mixture of polymers PN+F (intake of 1.8-2.9 g m^{-2}) repelled castor oil most of all. In Fig. 9h, the castor oil footprint on laminated paper with a polypropylene foil is presented, its degree of oil repellency (R6) is similar as the paper sized with the mixture of polymers P+F (R7). In the case of laminated paper with a polypropylene foil of thickness 42 μm with the basis weight 38 g m^{-2}, a physical barrier was created.

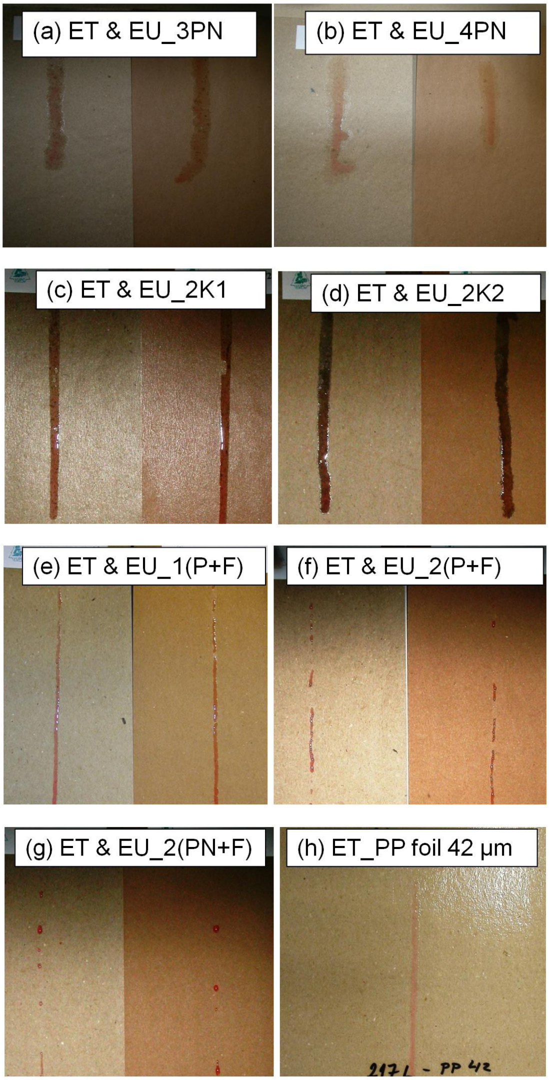

Fig. 9: Images of castor oil footprints on inclined surfaces of sized paper E and paper laminated with polypropylene foil after 1 hour after contact; intake of polymers on the sized side: (a) film forming polymer PN, 2.3-2.4 g m^{-2}; (b) film forming polymer PN, 2.8 g m^{-2}; (c) commercial mixture of polymers K1, 4.5-6.8 g m^{-2}; (d) commercial mixture of polymers K2, 1.4-2.5 g m^{-2}; (e) mixture of polymers P+F, 0.6-1.0 g m^{-2}; (f) mixture of polymers P+F, 1.1-1.8 g m^{-2}; (g) mixture of polymers PN+F, 1.8-2.9 g m^{-2}; (h) polypropylene foil, thickness 42 µm (38 g m^{-2}).

Tab. 2 presents the contact angle change of castor oil on the surfaces of base and sized papers H and E at times of 0.5 ms (SCA$_0$), 5 s (DCA$_5$) and 30 minutes (DCA$_{1800}$).

Tab. 2: Contact angle of castor oil and its change over the specified time.

Papers	Base	Sized with PVOH	Sized with the mixture of PVOH and polymer F
SCA_0 (°)	67-80	69-79	91-112
DCA_5 (°)	45-51	41-45	89-112
DCA_{1800} (°)	12-30	6-25	77-112

Contact angles of castor oil and their change over the specified time on base papers and papers sized with the aqueous dispersions of polyvinyl alcohol P and PN were quite similar. Paper surfaces with a contact angle between 10° and 90° are oleophilic and below 10° are superoleophilic. The free surface energy of these papers which was between 36 mJ m^{-2} and 42 mJ m^{-2} was higher than the surface energy of castor oil (34.5 mJ m^{-2}). Castor oil immediately wetted the surface of papers, feathered on the surface and subsequently penetrated into paper. After sizing the paper with mixtures of PVOH and fluorinated polymer, the contact angles of castor oil increased significantly and their changes over time were relatively low. Paper surfaces with contact angles between 90° and 150° are considered as oleophobic. Depending on the content of fluorinated polymer F on the paper surface, the free surface energy of the sized papers decreased to 21-30 mJ m^{-2} and the intensity of oil feathering and penetration were suppressed (Fig. 9).

Two-sided sized paper

The castor oil penetration time was measured on each side when evaluating of two- sided sized paper. The influence of paper, the composition of the aqueous dispersion and the number of passings through the size press on the penetration time of castor oil is presented in Tab. 3. The penetration time of castor oil was measured by the visual method when oil footprints appeared on the opposite side.

Sized papers are sorted by penetration time into 4 groups. In the first group (with a penetration time under 4 h), twofold sized paper E with 7% solution of film forming polymer PN, whose total intake was 3.5 g m^{-2} was included. In the second group (up to 6 h), threefold and fourfold sized paper H with 4% solution of film forming polymer P with the total intake 1.9-2.0 g m^{-2} was included. The third group (up to 24 h) includes paper H sized with the mixture of polymers P+F and the total intake of 1.4 g m^{-2}; further paper E sized with the mixture of polymers PN+F and the total intake 1.9 g m^{-2}; and finally paper E fourfold sized with film forming polymer PN and the total intake up to 5.4 g m^{-2}. In the fourth group (more than 48 h), paper H twofold sized with the mixture of polymers P+F and the total intake 2.6 g m^{-2}; and twofold sized paper E with the mixture polymers PN+F and the total intake 5.7 g m^{-2} were included. The castor oil penetration time of single sized papers with film forming polymers PN and P was considerably lower (less than 2 hours), therefore these papers were not included in Tab. 3. For the same reasons, the results of sizing with commercial aqueous dispersions of polymers K1 and K2 and the total intake 13.2 g m^{-2} and 5.2 g m^{-2} were also not included in Tab. 3.

Tab. 3: Influence of paper and sizing method with aqueous dispersions of different compositions on the penetration time of castor oil.

Penetration time of castor oil of two-sided sized papers H and E				
	Less than 4 hours	Up 6 hours	Up 24 hours	More than 48 hours
Paper, side and sizing	ET_2PN EU_2PN	HT_3P	HT_1(P+F)	HU_2(P+F)
Polymers intake on one side and **on both sides together** (g m^{-2})	1.7 – 1.8 **3.5**	0.7 **1.9**	0.83 **1.4**	1.1 **2.6**
Paper, side and sizing		HU_4P	ET_1(PN+F)	ET_2(PN+F)
Polymers intake on one side and **on both sides together** (g m^{-2})		1.0 **2.0**	0.96 **1.9**	2.9 **5.7**
Paper, side and sizing			ET_4PN	EU_2(PN+F)
Polymers intake on one side and **on both sides together** (g m^{-2})			2.7 **5.4**	2.8 **5.7**

Fig. 10 shows the influence of polyvinyl alcohols P and PN intake at two-sided sizing of papers E and H on the penetration time of the diluted maize oil (viscosity 2.7 mPa s) determined by the objective method using HST photometer.

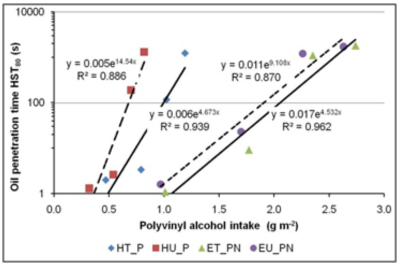

Fig. 10: Influence of polyvinyl alcohols P and PN intake at two-sided sizing of papers E and H on penetration time of diluted maize oil determined by the objective method using HST photometer.

The penetration time of oil increased with the intake of polyvinyl alcohol. The penetration time of oil measured on top side T and underside U was different, therefore in Fig. 10, intake of polyvinyl alcohol is specified for each side separately. Two-sided sized papers with a high intake of polyvinyl alcohol had very long penetration time of maize oil (1800 s). Therefore, this method was not used for evaluation of papers have been sized with mixture of film forming and fluorinated polymers, which had higher oil and grease resistance.

CONCLUSIONS

One-sided sized papers with resistance to grease in the range of values Kit 7 to Kit 9 were prepared with an aqueous dispersion of the film forming polymer polyvinyl alcohol. The applied amount of polyvinyl alcohol needed to achieve this degree of grease resistance was dependent on the porosity of the paper. For the sizing of paper with the higher content of fine surface pores of 0.7-5.4 s, polyvinyl alcohol intake between 0.8-1.2 g m^{-2} was required. At this intake of polyvinyl alcohol, sized paper had absorptiveness of castor oil Cobb_{120} 4.5-6.0 g m^{-2}. The same grease resistance was achieved for more porous paper (with a lower content of fine surface pores of 0.2-0.25 s) at a significantly higher polyvinyl alcohol intake of 2.5-2.7 g m^{-2}, while the absorptiveness of castor oil Cobb_{120} was 7.5-8.0 g m^{-2}.

One-sided sized papers with higher grease resistance (Kit 12) were prepared with the mixtures of film forming polymer with fluorinated polymer. The applied amount of polymers mixtures required to achieve this degree of grease resistance was depended on the porosity of the paper. For paper with the higher content of fine surface pores of 5.4 s, the intake of polymers mixture of about 1 g m^{-2} was required. With this intake of polymers mixture, the sized paper had the absorptiveness of castor oil Cobb_{120} of 2.4-4.0 g m^{-2}. The same grease resistance was also achieved even with more porous paper at a significantly higher intake of the polymers mixture of 2.7 g m^{-2} and the absorptiveness of castor oil Cobb_{120} was 5.5-6.5 g m^{-2}.

By adding of 200 ppm silver nanoparticles to the polymers mixture at sizing of porous paper, the grease resistance Kit of 8.5 and the absorptiveness of castor oil Cobb_{120} 7.3 g m^{-2} were reached already at intake 0.9 g m^{-2}. The barrier properties of paper sized only with the film forming polymer polyvinyl alcohol or its mixture with fluorinated polymer at intake 0.95 g m^{-2} were significantly lower (Kit 3 or Kit 7, Cobb_{120} 9.3 or 9.7 g m^{-2}). Addition of silver nanoparticles enabled to decrease the consumption of polymers while improving the resistance of porous paper against oil and grease. By using silver nanoparticles, it is possible to decrease the content of fluorinated polymer in the aqueous dispersion, which has a positive environmental impact.

Increase of castor oil penetration time to more than 48 hours was achieved only in the case of two-sided sized papers with aqueous dispersions composed of polyvinyl alcohol and fluorinated polymer. The intake of polymers when sizing paper with higher content of fine surface pores was 2.6 g m^{-2}, and in the case of paper with lower content of fine surface pores was up to 5.7 g m^{-2}.

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*Juraj Gigac, Monika Stankovská, Mária Fišerová
Pulp and Paper Research Institute
Dúbravská Cesta 14
841 04 Bratislava
Slovak Republic
*Corresponding author: gigac@vupc.sk