Greaseproof Paper Products: A Review Emphasizing Ecofriendly Approaches

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A cost-effective, eco-friendly, and health-promoting packaging system that prevents the passage of greases and oils would fulfill an urgent need. This review discusses what is known about the highly divergent technological paths that have been studied to achieve these objectives. Before the emergence of plastic films, the paper industry addressed these objectives in two ways, by parchmentizing and by high levels of refining of the fibers. Parchmentizing means passing the paper through a bath of concentrated sulfuric acid, followed by rinsing out the acid and drying the sheet. Though both parchmentized paper and highly refined greaseproof paper products are still made, they have been substantially displaced by oil-repellent fluorocarbon treatments of paper. The fluorocarbon treatments have allowed papermakers to achieve greaseproof properties with ordinary paper machine equipment at ordinary refining levels and without a need to immerse the paper in strong acid. Now, however, due to environmental concerns and regulations, the paper industry needs more options. Some promising directions in published research include advances in chemistry, superoleophobic surfaces, nanocellulose films, and systems to protect nanocellulose films from the effects of moisture.

Keywords: Fluorocarbons; Perfluorocarbons; Vegetable parchment; Glassine paper; Oil resistance; Nanocellulose; Butter paper; Fast food packaging

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INTRODUCTION

Motivation

An early patent called for the treatment of paper with casein, glycerol, and sugar to make it resistant to grease (Wright 1922). The motivation was to be able to use paper – an inexpensive commodity product – as a convenient packaging material for greasy foods. The greaseproof market segment includes baking papers (sometimes regarded as a type of glassine paper), butter papers (which can include vegetable parchment), and packaging products for various oils (MarketWatch 2019). Various uses of vegetable parchment have been described (Ahlstrom Muksjo 2019). The market size of greaseproof paper has been projected to reach about $1.1 billion by 2025 (Acumen 2019).

Despite past market growth and optimistic projections for the future, greaseproof paper is facing some serious challenges. Much of the uncertainty involves the use of fluorochemicals, which are now widely used to impart resistance to grease and oils (Kissa 2001; Hagiopol and Johnston 2012). The term "perfluoro" is used when all the hydrogens on an alkyl chain have been replaced by fluorine atoms. The health effects of fluorinated materials are a concern, especially in cases where the paper products come into contact with food (Birnbaum and Grandjean 2015; Blum *et al.* 2015; Mudumbi *et al.* 2017). Fluorinated compounds attributable to greaseproof treatments of paper products have been found in sludge from municipal wastewater treatment (Lee *et al.* 2010). Concerns about the persistence and toxicity of perfluorochemical compounds have been expressed by scientists (Blum *et al.* 2015). Some greaseproof papers currently supplied have been formulated to be 100% biodegradable, avoiding the use of fluorochemicals (NordicPaper 2019). Greaseproof paper products also face cost pressures, which threaten their ability to compete against such alternative materials as polyethylene films (Giatti 1996; Acumen 2019).

Directions of Technological Advances for Greaseproof Paper

All of the issues just mentioned, in addition to concerns about biodegradability (Kumar *et al.* 2014; Kisonen *et al.* 2015), have provided motivations for innovations in greaseproof paper products. Recent advances have involved such aspects as alternative chemistries, new application strategies, and approaches that involve the use of nanocellulose. However, to lay groundwork for understanding recent and potential future innovations in the field, this review of the literature starts by considering health and environmental issues associated with the currently very important fluorochemical-based greaseproof products, then a review of how such products are employed in making paper products. Some general comments regarding the application strategy of fluorocarbon-based products, mainly referring to their improved retention at the wet end of paper machines, are also considered.

Next to be discussed is the topic of superoleophobicity, which uses nanostructures as a means of amplifying effects of fluorochemicals. After that, the focus of this review shifts to alternative approaches, *i.e.* ways to achieve greaseproof performance without use of fluorochemicals. Two of the most viable and still economically relevant alternatives, parchmentized paper and glassine paper, actually pre-date the introduction of fluorochemicals. Both these approaches rely on the preparation of extremely dense paper, using two completely different strategies. A grade called natural greaseproof paper is similar to glassine (heavily refined), but not supercalendered. The most recent trend, achieving greaseproof paper by strategic use of nanocellulose, likewise involves the formation of very dense, almost impermeable layers. Each of the approaches to achieving resistance of greases and oils has its advantages and challenges, and the goal of this review article is to provide a starting point for further innovations.

OVERVIEW OF HEALTH AND REGULATORY ISSUES

Environmental Concerns Regarding Fluorocarbons in Greaseproof

Health and regulatory issues deserve to be discussed early, since, to a greater extent than other issues, changes in future regulations and industry practices have the potential to bring about abrupt changes in the greaseproof paper market. Though it is possible that such changes might provide a favorable environment for the development and growth of alternative technologies, such technologies will take time to develop and implement.

Fluorochemicals are unlike anything found in nature. An alkyl chain in which essentially all of the hydrogens have been replaced by fluorine atoms (*i.e.* perfluorinated) presents an extremely low energy of interaction with its surroundings. The high electronegativity of fluorine causes it to hold tightly to its electrons. As a consequence, the dispersion component of van der Waals forces is far lower than any natural surface (Garbassi *et al.* 1994; Castner and Grainger 2001). On the positive side, this situation makes it possible for humans to enjoy such products as non-stick frying pans, sealing tape for plumbing connections, and greaseproof containers, especially for fast foods. But on the negative side, perfluorinated compounds products are very persistent in the environment (Mudumbi *et al.* 2017). Those compounds also have been associated with increased risks of cancers, developmental toxicity, immunotoxicity, and metabolic disruption (Schaider *et al.* 2017; Tokronov *et al.* 2019).

When fluorochemical treatments are applied to paper and other surfaces, they do not necessarily stay there (Alexander *et al.* 2008; Trier *et al.* 2011a). For instance, they can migrate into simulated food (D'Eon *et al.* 2009). They also have been found in the sludge of wastewater treatment plants (Lee *et al.* 2010). Recently Tokranov *et al.* (2019) showed that X-ray photoelectron spectroscopy (XPS) can be used to rapidly and definitively quantify levels of perfluorinated compounds at the surfaces of paper and other materials. They also can be quantified in solution, including after extraction of solids with a solvent, by use of high-performance liquid chromatography coupled with time-of-flight mass spectrometry (Trier *et al.* (2011b) or with conventional mass spectrometry (Zabeleta *et al.* 2016). The latter authors were able to distinguish fourteen different perfluorocarbon compounds and ten related compounds in a variety of fast-food packages, such as popcorn bags.

The biodegradability of perfluorocarbons still requires more comprehensive study. Lee *et al.* (2010) showed that a variety of reaction paths can lead to breakdown of certain perfluorocarbons that they studied. By identification of breakdown products, they were able to conclude that several mechanisms of degradation must have been involved, including a beta-oxidation pathway.

Regulations Affecting Perfluorocarbons in Paper Products

When the health effects and high persistence of perfluorinated compounds became widely known, US manufacturers of those products came to an agreement with the US Environmental Protection Agency (USEPA) to stop production of a specific class of those compounds that had been identified as being the most resistant to biodegradation, the long-chain perfluorocarbons (Wang *et al.* 2013; Rice 2015; Schaider *et al.* 2017). Analogs having eight-carbon chains have been shown to accumulate in animal tissues (Kabadi *et al.* 2018), so shorter chains are now used in the US. The six-carbon perfluorocarbon compounds do not appear to have the same biopersistence and potent toxicity as the longer-chain versions (Rice 2015). However, the long-chain products, though not made in the US, continue to be made and used elsewhere in the world (Schaider *et al.* 2017). Regulations, and the uncertainty regarding future regulations have led to interest in perfluorocarbon-free systems for greaseproofing of paper (Anon 2017).

FLUOROCARBON TECHNOLOGY FOR GREASEPROOF PAPER

With the exception of some traditional greaseproof paper products for baking and for the wrapping of butter and cheese (covered in a later section), the current greaseproof market is dominated by perfluorinated paper products, which are considered in this section. Such products rely on a simple strategy: cause the free energy of the paper surface to be so low that not even a grease or oil will spread on it. The general field has been described in earlier review articles and monographs (Castner and Grainger 2001; Kissa 2001; Hagiopol and Johnston 2012).

Testing Methods for Grease Resistance

To lay the groundwork for a discussion of this class of greaseproof products (as well as some of the other greaseproofing technologies to be described later), the testing procedures are considered first.

Standard methods

The most accepted way to evaluate greaseproof papers that have been treated in some way with perfluorinated compounds is called the kit test, which is specified in TAPPI Method T559 cm-02 (TAPPI 2002). This test uses a series of 12 solutions with different ratios of caster oil to toluene to n-heptane. The aggressiveness of the test solutions increases with increasing content of heptane and decreasing content of caster oil.

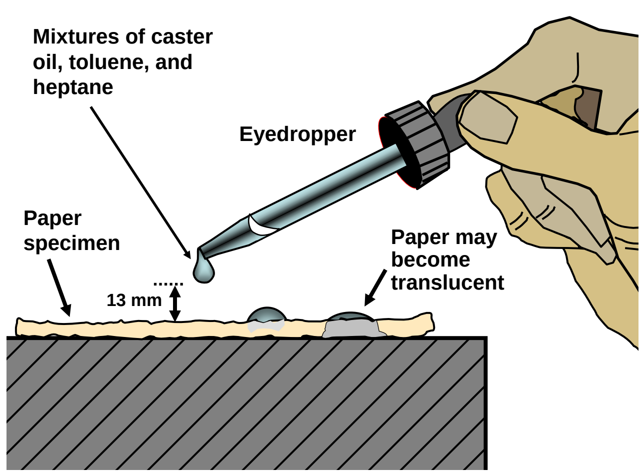


Fig. 1. Schematic illustration of the "kit test" (TAPPI Method T559) for determination of the extent of resistance to grease penetration

As illustrated in Fig. 1, the tester uses an eye-dropper to place a drop of a selected solution, usually of intermediate “kit number”, from a height of about 13 mm onto a sheet of the subject paper resting on a clean, dark surface. After 15 s the droplet is wiped away, and any darkening of the underlying area, which would be attributed to filling of the paper’s voids with the test fluid, implies “failure” of the test. The tester continues until determining the highest kit number corresponding to a “pass”.

Contact angles

Because the mechanism by which the fluorochemical agents work involves wettability, measurements of contact angles can provide relevant information. Aulin *et al.* (2008) reported a strong correlation between contact angles and the concentration of fluorine at paper surfaces.

Contact angle tests can be carried out in a way to distinguish between the contributions of dispersion forces (relevant for all surfaces, but reduced in magnitude on perfluorinated surfaces) and polar and hydrogen bonding forces to the free energy of the surface. The latter give rise to much higher surface energy in the presence of, for instance, -OH groups at a surface of interest. The relationship between contact angles and surface energy on cellulose-related surfaces has been reviewed (Hubbe *et al.* 2015). Briefly stated, the way to obtain separate information for both nonpolar and polar contributions to surface free energy entails comparing the contact angle values for two probe liquids, one nonpolar and one polar (Owens and Wendt 1969).

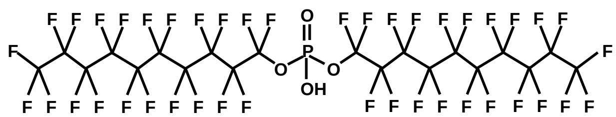
In theory, if the contact angle of a liquid on a solid is greater than 90 degrees, then that liquid will be unable to pass into pores of the material, which are often modeled as ideal smooth cylinders (Lucas 1918; Washburn 1921). This concept depends on an assumption that the surfaces within the tiny pores have the same affinity characteristics as the external surface, at which the contact angle is evaluated. An important prediction of the so-called Lucas-Washburn concept is that resistance to passage of liquids through porous solids is strongly favored by small pore diameters. In principle, this could be achieved by extensive refining of pulp fibers, thus producing a very dense sheet of paper (see further discussion in a later part of this article). However, heavy refining of the pulp would greatly increase the effective surface area to be covered by the perfluorinated agent, thus driving up the cost of treatment. The relationship can be unpredictable, however, because the effective surface area of refined kraft fibers decreases drastically during the process of drying, and the hydrophobic agent generally becomes spread out on the external surfaces only after the paper has become at least partly dried (Hubbe 2014). Heavy refining also slows down the rate of dewatering, often slowing the production rate of papermaking. Thus, the degree of refining needs to be optimized in each case.

Conventional Fluorocarbon-based Grease-barrier Technologies

Fluorochemical options

For conventional perfluorocarbon treatment of paper, the oil-repellent agent can be added either to the surface of the paper or to a suspension of fibers before the formation of the sheet (Giatti 1996, 1997). In the latter case, monomeric agents are typically applied. Kissa (2001) has provided a listing of the extensive patent literature covering such products. For addition to the fiber slurry, perfluoroalkyl phosphates (PAPs) are widely used (Trouve and Delperdande 1995; Lee *et al.* 2010; Trier *et al.* 2011a,b; Hagiopol and Johnston 2012; Zabaleta *et al.* 2016). Two examples are shown in Fig. 2 (Trier *et al.* 2011a; Zabaleta *et al.* 2016). Aulin *et al.* (2008) mention some alternative monomeric fluorochemicals that also could be used, such as perfluoro-octadecanoic acid or the reactive agent pentadecafluoro-octanoyl chloride.

Sodium bis (1H, 1H, 2H, 2H-perfluorodecyl) phosphate



Perfluorodecyl phosphonic acid

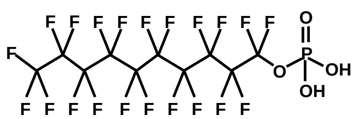


Fig. 2. Chemical structures of two representative perfluorinated monomers for addition to the fiber slurry in the production of greaseproof papers

Polymeric

Copolymers having perfluorinated groups are also widely used, especially for the surface treatment of paper (Konig *et al.* 1985; Claude 1997; Corpart *et al.* 1997; Hupfield *et al.* 2011; Hagiopol and Johnston 2012). Examples of polymeric products added to the paper surface to achieve greaseproof performance are listed in Table 1.

Table 1. Examples of Fluorinated Copolymers that Have Been Added to Paper Surfaces to Convey Greaseproofness

Type of Polymer	Reference
Emulsions prepared by graft copolymerization of ethylenically unsaturated perfluoroalkyl dispersions onto acrylate dispersions	Konig *et al.* 1985
Fluorinated acrylic copolymer with glyoxal or a compound containing glyoxal	Claude 1997
Fluorinated acrylic copolymer with glyoxal or polyamide-epichlorohydrin resin	Corpart *et al.* 1997
Anionic perfluoropolyethers used with nonionic starch	Iengo & Gavezotti 2009
Copolymer of fluorine-containing monomer and a mercapto group-containing organo-polysiloxane	Hupfield *et al.* 2011
Listing of some additional relevant patented copolymers	Hagiopol & Johnston 2012

Surface application

Because fluorochemical treatment of paper is intended to affect paper's outer surface, it makes logical sense to apply it at a size press or by using other equipment that enables surface application (Szymanski and Ingeilewicz 1995; Giatti 1996; 1997). In such applications it is common to employ a copolymer with perfluorinated side-chains in combination with other polymers such as anionic starch or carboxymethylcellulose (CMC) (Szymanski and Ingeilewicz 1995; Giatti 1996, 1997; Kissa 2001). As in the case of copolymeric size press additives that are used to increase paper's resistance to aqueous fluids, it is reasonable to expect that there is migration of low-energy polymer segments to the solid-air interface in the course of drying (Garnier *et al.* 2000; Hubbe 2007; Khayet and Essalhi 2015). This arrangement achieves favorable free energy of the system. For such a treatment to work effectively, one relies upon an assumption that the polymer nano-scale arrangement reached during the process of drying does not easily change again when the surfaces are exposed to liquids. Unlike monomeric sizing agents, there is no evidence of the involvement of an anchoring system, *e.g.* with alum or covalent bond formation.

Surface-sizing treatments can be sensitive to the presence of certain ionic materials that appear to destabilize the solutions. For example, water hardness due to the presence of calcium or magnesium ions can be harmful (Giatti 1997). A chelating agent can be used in such cases to tie up the offending ions.

The performance of a greaseproof copolymer mixture applied to the paper surface can be enhanced or made more cost-effective by the incorporation of various additives. For example, wax is often added to such formulations (Kissa 2001). Crosslinking agents are also used, presumably with the intention of keeping the barrier layer intact even when the material is in the proximity of aqueous solution (Hagiopol and Johnston 2012). Glyoxal and various conventional wet-strength agents have been used to achieve crosslinking (Corpart *et al.* 1997). Another promising additive to be considered for inclusion in formulation of fluorochemical treatments for the paper surface would be montmorillonite (*i.e.* nanoclay), or related highly platy mineral products that have been used in other approaches to achieving grease resistance (Girard and Trillat 1996; Perng and Wang 2012; Olsson *et al.* 2014; Rosen *et al.* 2017). Almgren (1980) refers to the use of silicones and chromium stearate in decorative laminates to improve their grease-resistance.

It is important to keep in mind that the success of any surface treatment of paper is invariably linked to attributes of the base sheet. For instance, it can be important to size the base sheet with alkylketene dimer (AKD) or other hydrophobic agents to efficiently keep the size-press formulation near the surface of the paper (Giatti 1996, 1997). Also, logic would suggest that a smooth sheet with relatively small pore openings would be helpful in reducing the required amount of greaseproof formulation that would need to be applied to the surface of the sheet. An unexpected effect of the type of fiber used in the base sheet on the performance of fluorochemicals was studied by Yang *et al.* (1999). It was found that mechanical pulp furnish was more difficult to render grease-resistant in comparison to the more commonly utilized kraft pulp fibers. The difference was found to be due to the much higher levels of pitch-like "extractives" in the mechanical pulp. The cited researchers were able to overcome the problem by the incorporation of hydrophobically modified starch in the size-press formulation.

Plasma fluorination

Besides using the size-press, another possible way to apply a highly grease-resistant coating to paper would be by using a plasma. For example, plasma conditions can be used to polymerize monomers such as pentafluoroethane and octafluorocyclobutane in the presence of cellulosic surfaces (Vaswani *et al.* 2005). Such an approach is worth considering because plasmas have a wide range of energy (*i.e.* cold plasma *vs.* thermal plasmas) and a wide range of optional carrier gas composition. Cold plasmas, in which only a small fraction of the molecules are in a high energy state, have been employed for food packaging (Ekezie *et al.* 2017). The surfaces to be treated can be plasma-treated in a continuous process, and the high-energy molecules, such as free-radical species, can promote very fast reactions to derivatize the material being treated.

Addition to the paper furnish

In many situations it may be advantageous to add a suitable fluorochemical agent to the fiber suspension before the formation of the paper (Vitek 1975; Giatti 1996, 1997; Perng and Wang 2004). For instance, some products such as three-dimensionally formed paper plates do not include size-press treatment option. The required dosage of chemical to be added to the fiber slurry may be higher than for size-press treatment. A higher level of fluorochemical may be needed, especially if the wet-end mixture contains mineral fillers, which typically have a relatively high surface area (Giatti 1996). Because the phosphate-type perfluorinated monomers commonly used in such applications bear a negative ionic charge, it is generally recommended to pretreat the fiber furnish with a suitable cationic additive (Giatti 1996, 1997; Perng and Wang 2004). In addition, a hydrophobic sizing agent, such as alkylketene dimer (AKD) is recommended so that the product can avoid becoming soaked by water (Giatti 1996; Perng and Wang 2004). Finally, a retention aid, such as very-high-mass copolymer of acrylamide with acrylic acid, is recommended to efficiently retain the other additives (Giatti 1996; Perng and Wang 2004). It is reasonable to expect similar effects with cationic acrylamide copolymer retention aids, which are more commonly employed in the industry. Various approaches should be considered regarding the selection of the dosing point of the perfluorochemical (thick stock *vs*. thin stock), single addition *vs*. split feeding, co-addition of fixative (high charge cationic polymers), and the addition point of starch. Significant differences in the final grease proofing level were observed in the lab for different modes of the addition of fluorocarbon products with their dosage kept constant (Pruszynski 2015). The resistance to grease penetration varied in a wide range, as indicated by passing the penetration test between oil #3 to #6 of the test kit. Detailed lab testing to determine the best application strategy of fluorocarbon products may identify potential improvements in their performance and are strongly recommended even for already running applications.

Super-phobicity

A technology called super-oleophobicity offers a way to make fluorocarbon-type treatments more effective. Such a strategy was demonstrated by Jiang *et al.* (2016), who used a debonding agent during paper preparation, followed by oxygen plasma treatment, and finally by fluorosiline treatment. Promising results also have been obtained with plasma etching of paper followed by perfluorochemical treatment (Li *et al.* 2013; Jiang *et al.* 2017). The mechanism of super-oleophobicity has been reviewed (Song and Rojas 2013; Hubbe *et al.* 2015). Super-oleophobic systems work in a manner that is analogous to that employed by lotus leaves, which can remain mostly dry even when directly exposed to a heavy rainstorm while floating on water. All such systems, whether they are repelling aqueous fluids or something else, rely upon a combination of two features, one involving roughness and the other involving surface free energy. The necessary roughness can be advantageously achieved by depositing a layer of nanoparticles onto the surface. These two features working together are illustrated together in Fig. 3. The figure shows schematically how the deposition of nanoparticles can provide a very high level of roughness at a tiny scale, while a final coating with a monomolecular layer of a low-energy material affects the local value of contact angle (Aulin *et al.* 2009). As illustrated, a super-phobic situation arises in cases in which the fluid is essentially being held out on the points of fine-scale roughness. The main distinction between a super-oleophilic surface and an "ordinary" super-hydrophobic surface is that the low-energy substance is a fluorinated compound. The mathematical relationships underlying such effects were derived by Cassie and Baxter (1944). Care must be taken to use the correct form of the governing equation (Milne and Amirfazli 2012).

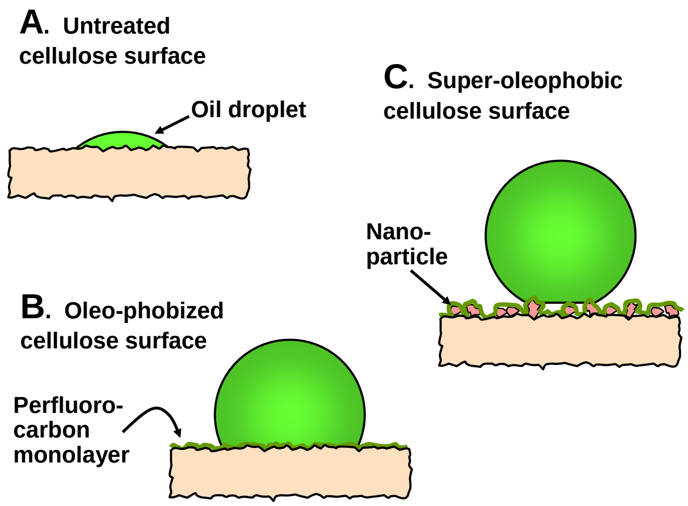


Fig. 3. Schematic illustration of a super-phobic system that employs fine-scaled roughness in combination with a low surface free energy to create very high levels of resistance to oils

GREASEPROOF TECHNOLOGIES WITH HIGH-DENSITY PAPER

Historical Notes

Because of ongoing concerns about the toxicity and persistence of fluorocarbons, even when they are restricted to carbon chain lengths of six or less (Wang *et al.* 2013; Schaider *et al.* 2017), it is important to keep in mind the known alternative approaches. The good news is that some of those approaches are still widely practiced at an industrial scale. On the other hand, there is a continuing need to advance the technologies to achieve greater cost-effectiveness and better meet customer needs.

Starting long before the invention of fluorocarbon compounds in the 1950s (Kissa 2001), there already were greaseproof papers being developed and sold (Wright 1922; Blasweiler 1924; Arnot 1931; Giatti 1997). Since none of these products had a means of resisting wetting by greases and oils, they had to rely on a different mechanism, which was essentially that of providing a highly dense, impenetrable layer. The two traditional ways of achieving high-density paper, namely parchmentizing and glassine, are considered in this section.

Parchmentized Paper

A product that has been variously called vegetable parchment, parchmentized paper, papyrene, or butter paper has been known for about 150 years (Mayer 1860). Densification is achieved by passing a paper sheet though a solution of sulfuric acid, following by passing it through a neutral bath of water and drying. The process is illustrated schematically in Fig. 4. The strong acid causes the fibers to swell, forming a homogeneous sheet (Meinander 2000). Hidayat *et al.* (1996) employed 70% sulfuric acid solution at temperatures of 15 to 20 °C for 10 to 20 seconds, and they used a weak ammonia solution for neutralization. Sachsenroeder (1902) claimed an early innovation whereby a sheet of paper that had just been passed through a sulfuric acid bath was joined to an untreated sheet, and the two were passed through a squeezing nip before the water bath. Thus it is feasible to acidify only part of the product, and the dense and brittle part can be supported by ordinary paper.

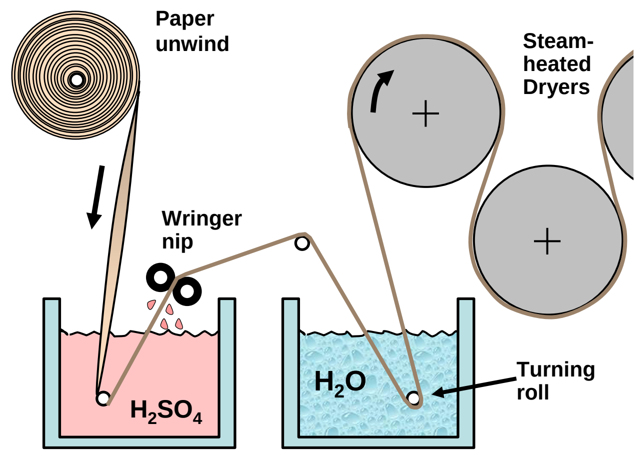


Fig. 4. Schematic illustration of parchmentizing process

Parchmentized paper continues to be used for packaging of high-end butter and cheese products (Slott-Moller 1972; Lechiffre 1992; Giatti 1996). A distinguishing feature of parchmentized paper is that it does not have a non-stick surface, so that in its default form it is not recommended for baking (MetaTissue 2019). However, a parchmentized paper suitable for baking can be prepared by silicone coating (Ahlstrom Muksjo 2019).

Conventional Highly Refined Greaseproof Paper (Glassine)

Refining

As an alternative to immersion of paper into concentrated sulfuric acid, papermakers learned that they also could achieve very high density, thereby preventing the penetration of greases and oils, by extensive refining, especially in the case of sulfite pulps (Griffin 1976; Norris 1978; Giatti 1996; Kjellgren and Engstrom 2005; Kjellgren *et al.* 2006, 2008; Song *et al.* 2015). As noted earlier, the term natural greaseproof paper has been used for paper made from highly refined pulp by without supercalendering. Notably, a high level of refining also was found to benefit the holdout properties of paper prepared with a fluorochemical added to the furnish (Perng and Wang 2012). Dense grease-resistant papers are well known commercial products (Steindorf 1977), although they have come under heavy competition from plastics. Glassine baking papers having a non-stick quality are a sizeable market segment (Giatti 1996; Acumen 2019; MetsaTissue 2019).

The reason that highly refined chemical pulp fibers can resist grease can be attributed not only to the high density of such paper layers but also to the extensive and well-organized hydrogen bonding that occurs between cellulosic surfaces dried while remaining in contact. Figure 5 provides a schematic illustration of this concept. The idea is that the relatively high energy of a hydrogen bond, in comparison to the dispersion component of van der Waals forces, means that cellulosic and related polysaccharide barrier layers can be more effective in comparison to such plastics as polyethylene, which are bound together only by the weaker class of forces.

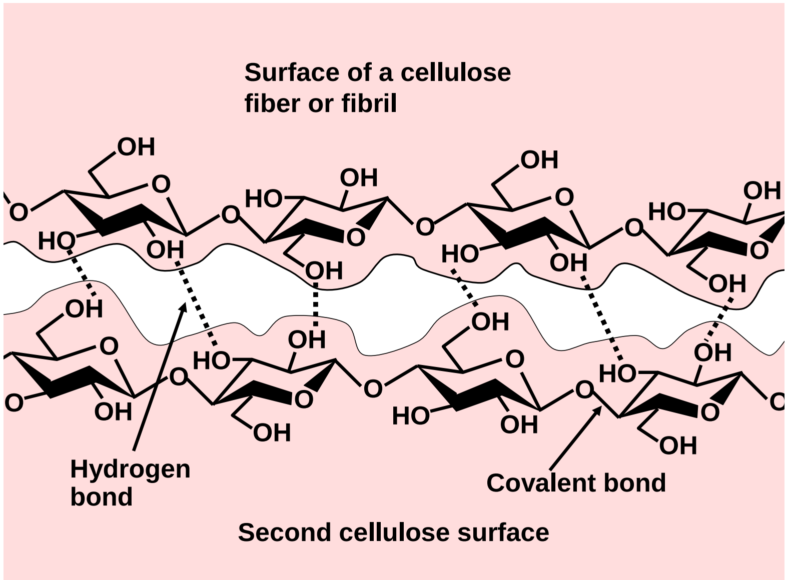


Fig. 5. Schematic illustration of how hydrogen bonds can be expected to form between adjacent cellulose-containing solids that are dried in contact with each other

The high energy requirement has been noted as a primary concern associated with the preparation of glassine paper (Szymanski and Ingielewicz 1995; Meinander 2000; Kjellgren and Engstrom 2005). Kjellgren and Engstrom (2005) reported that the required amount of refining could be decreased by application of hydrophilic polymers at the size press, followed by calendering (see later). The other thing that glassine product manufacturing is known for is very long Fourdrinier dewatering zones, associated with the relatively slow rates of drainage. The slow drainage can only partly be compensated by advances in mechanical dewatering equipment (Anon. 1970). It has been shown that the refining requirement can be reduced by at least 10% by pretreating the pulp with a cellulase enzyme mixture (Yamaguchi and Yaguchi 1996). Lu *et al.* (2016) likewise showed that the preparation of greaseproof paper could be facilitated by cellulase treatment before extensive refining of the pulp.

Other pulps

Glassine papers having grease resistance also can be produced from some less-considered fiber sources. These include banana pseudostem (Saikia *et al.* 1997; Goswami *et al.* 2008; Rajput 2009). Goswami *et al.* (2008) proposed that a high amount of gums and mucilage in the banana biomass contributed to its favorable performance. Water hyacinth also was used for preparing greaseproof paper, starting with a soda pulping (Goswami and Sakia 1994). Pei *et al.* (2013) likewise showed that algal biomass can be used. Rai *et al.* (1995) compared poplar chips of different age groups for the preparation of kraft pulp used in greaseproof products. Wood from the oldest trees yielded the highest resistance to grease. In considering these reports, it is worth noting that the starting properties of woody material yielding favorable properties for glassine paper might be quite different compared to other grades of paper, for which there is usually more emphasis on paper strength rather than resistance to penetration.

Wet-end addition or coating with platy minerals

Montmorillonite (MMT), which is sometimes known as bentonite or nanoclay, can be prepared so that extremely thin platelets (< 10 nm) separate from each other (Knudson 1995). Inclusion of such particles within a paper structure has been shown to block the flow of both air and oils (Perng and Wang 2012; Rosen *et al.* 2017). Such results can be explained by the tendency of tiny plate-like particles to plug the pores of a very dense paper sheet. Another way to explain this is to say that the molecules passing through the paper have to take a longer path, *i.e.*, increased tortuosity. It is worth noting that the advantage of using a highly platy mineral to decrease permeability of paper might sometimes increase the required level of fluid-resistant chemicals. That is because, as noted earlier, the high surface area per unit mass of mineral particles implies that a higher dosage may be needed to form a monolayer on the available solid surfaces.

Applying a layer of platy minerals to paper's surface is another option to enhance holdout. Hallam and Nutbeen (2012) showed that paper's resistance to permeability, in general, can be enhanced by coating it with specialized clay having a large particle size and a very high aspect ratio. Khairuddin *et al.* (2019) showed increases in grease resistance and water vapor permeability when paper was coated with a mixture of starch and bentonite clay. Related work has been reported by Andersson *et al.* (2002), Koivula *et al.* (2016), and Tsurko *et al.* (2017). More research is needed to determine whether such coatings can provide suitable greaseproof performance for products of interest.

Surface sizing

The performance of glassine-type based-sheets can be improved by applying various water-loving polymers to the surface. It is worth considering again the 1922 patent by Wright that was cited at the very start of this article. It is notable that the casein, glycerol, and sugar cited in that patent are all relatively hydrophilic, hydrogen-bondable substances. With an important exception, the fluorochemicals, the requirements of hydrogen bonding ability can be regarded as a consistent theme in the development of greaseproof paper systems over many years.

Table 2 lists published studies in which grease resistance was studied in response to surface addition of the indicated polymers. A common feature of the listed polymers is that all of them have a strong hydrogen bonding ability. Once a surface film on the paper has been dried, the hydrogen bonds can be expected to hold the polymeric chains together firmly, decreasing the probability that a molecule of a gas or grease can diffuse through the material. In some sense, hydrogen bonding performs the role of anchoring the polymeric material, which is crucial in the case of conventional sizing materials.

In addition to the components shown in Table 2, it also has been reported that the effectiveness of surface films for enhancing the grease resistance of glassine papers can be increased by crosslinking. For instance, the use of citric acid was mentioned in two studies (Olsson *et al.* 2014; Javed *et al.* 2017). In addition to its function as a dispersant, it seems likely that it also could have formed ester bond links, depending on the temperature of the drying process. Tayeb and Tajvidi (2019) showed that polyamidoamine-epichlorohydrin, a reactive wet-strength resin, can be used for greaseproof coatings.

The acrylate emulsion tested by Rosen *et al*. (2017) was found to work even better when formulated with a thickener, having similar chemistry as the emulsion, but having a non-crosslinked, long-chain structure. Further enhancement was obtained with the incorporation of plate-like mineral particles. Olsson *et al.* (2014) demonstrated positive effects of including montmorillonite in thermoplastic starch coatings to enhance resistance to oxygen. The platy mineral particles increase the average lengths of paths that molecules have to take when diffusing through the film. Other studies have shown a correlation between resistance to gas permeation and oil permeation (Aulin *et al.* 2010; Österberg *et al.* 2013; Kisonen *et al.* 2015).

Table 2. Studies of the Effects of Hydrophilic Polymer Surface Films to Enhance the Grease Resistance of Paper

Polymers Used	Selected Findings	Reference
Starch and PVOH	Patent claim, grease resistance.	Schwartz 1941
Starch, CMC	Correlation with air permeability.	Slott-Moller 1972
Starch, alginate, CMC	Filling the pores of the glassine paper.	Meinander 2000
Soy protein isolate	Grease resistance better than plastic.	Park *et al.* 2000
Various polymers	Focus on gas barrier by greaseproof.	Vähä-Nissi *et al.* 2001
Protein and starch	Patented greaseproof system.	Billmers *et al.* 2003
Chitosan, alginate	Aliginates gave the best results.	Ham-Pichavant *et al.* 2005
Starch, PVOH, PAMA	Oxidized starch; water resistance.	Jansson & J. 2006
Starch, hydrophobic	Optimization of greaseproof paper.	Jonhed & Jarnstrom 2009
Starch	Thermoplastic starch at pilot scale.	Olsson *et al.* 2014
Hydroxypropylcellulose	Oil resistance was achieved.	Leminen *et al.* 2015
Starch & alginate	Both additives separately effective.	Song *et al.* 2015
Starch & PVOH	The coating seals defects in the paper.	Javed *et al.* 2017
Acrylate emulsion	More effective than starch & PVOH.	Rosen *et al.* 2017
Chitosan & PDMS	Polydimethylsiloxane system.	Li & Rabnawaz 2019
Alginate, CMC, *etc.*	Grease resistance correlated to polarity.	Sheng *et al.* 2019

Notes: PVOH = poly-(vinyl alcohol); PAMA = poly-alkylmethacrylate; CMC = carboxymethyl cellulose

Calendering

Given the fact that glassine papers owe their barrier performance to their density, it makes logical sense to consider calendering. In other words, passage of the paper between nips of press rolls at very high pressure might be beneficial. The use of calendering in the production of greaseproof paper has been widely reported (Giatti 1996; Girard and Trillat 1996; Meinander 2000; Kjellgren and Engström 2005). Kjellgren and Engstrom (2005) found that calendering decreased the volume fraction of pores in the paper. Meinander (2000) specified supercalendering, a process in which the paper passes through multiple nips, each involving a combination of a hard roll and a soft roll. Supercalendering is known to apply shear to the paper surface, developing a high degree of smoothness, gloss, and density.

Protection from moisture

Most of the afore-mentioned studies of surface applications to enhance the grease-resistant performance of glassine paper did not involve a means of dealing with the potential effects of water on such systems. According to Javed *et al.* (2017), it is essential for a coating comprised of starch and PVOH to be protected on both sides from the effects of moisture.

The ultimate in protection against water might consist of plastic laminate layers, and in fact, that option has been considered for enhancing the barrier performance of dense cellulosic layers (Carlsson and Ström 1991; Park *et al.* 2000). Compared to the other coatings considered in this section, plastic laminates tend to be more expensive to prepare, not biodegradable, and not recyclable. A challenge for researchers in the coming years is to develop biodegradable and recyclable water barrier layers that can serve the same purpose cost-effectively, preserving the effectiveness of greaseproof layers even when wetted by aqueous fluids. As corporations work to find more environmentally friendly alternatives to existing products, there is a motivation to replace non-degradable plastic films in packages with biodegradable films.

Synergistic effect

In the course of studying polyethylene extruded coatings onto glassine paper, it was observed that the oxygen barrier performance of the combination greatly exceeded that of either of the layers by itself (Stolpe 1996; Kjellgren *et al.* 2008). These results were interpreted by assuming that the glassine paper is inherently an extremely effective barrier, but at the same time it contains isolated defects, consisting of pores allowing free access for the passage of molecules. It was proposed that a critical role of the extruded plastic layer was to plug up those isolated pores that happen to extend through the thickness of the glassine paper. There seems to be a need for follow-up work focusing on more efficient ways to plug up such defects, rather than the expensive and non-ecofriendly application of a laminate layer covering the entire surface.

GREASEPROOF SYSTEMS INVOLVING NANOCELLULOSE

The next logical step to consider, beyond the use of glassine paper with its highly refined fibers, is to refine the fibers much more extensively, until they become microfibrillated or nanofibrillated. Micro- and nanofibrillated cellulose (MNFC) products have been widely studied in recent years (Lavoine *et al.* 2012). Grease resistance of such systems has been reported in multiple studies (Aulin *et al.* 2009, 2010; Österberg *et al.* 2013; Kumar *et al.* 2014; Sirviö *et al.* 2014; Kisonen *et al.* 2015; Raghu 2015). Some options for using MNFC in greaseproof paper products will be considered later, after providing some necessary background.

To better understand these systems, some key concepts related to diffusion are reviewed, followed by a discussion of relevant research results relating to factors affecting diffusion of grease through nanocellulose films. The subsequent topics to be discussed include defects in nanocellulose films and their susceptibility to and protection against moisture. Finally, there will be a discussion of practical procedures by which nanocellulose can be incorporated into paper products to meet the requirements of grease-resistance.

Principles of Diffusion

To understand why a film prepared by the drying of micro- or nanofibrillated cellulose (MNFC) would be a superior barrier to grease and oils, the first point to consider is density. A very high density of the MNFC films was shown by electron microscopy (Aulin *et al.* 2010). The very high flexibility of the fibrils is expected due to their content of amorphous cellulose, while at the same time the high content of crystalline cellulose provides about 70% of the materials that allow no permeation at all (Hubbe *et al.* 2017a). The high cohesive energy density within such films, due to the extensive hydrogen bonding, means that the diffusion rate of nonpolar molecules through the solid material is extremely slow (Aulin *et al.* 2010). At the same time, the dependency of such films on hydrogen bonding can explain a strong drop-off in barrier properties when the relative humidity increases above about 65% (Österberg *et al.* 2013).

Tortuosity and its limitations

Tortuosity can be defined as the ratio between the perpendicular distance through a given film and the length of the path that a diffusing molecule would have to take through that film to get around impermeable particles, such as crystalline domains. Though the word tortuosity is often mentioned in published explanations of the ability of nanocellulose to serve as a barrier layer, it is important to keep in mind that the fibrillar shapes of most cellulosic fibrils and nanocrystals is not well suited for blocking the diffusion of molecules through a film (Hubbe *et al.* 2019). This point was brought out most clearly by Wolf *et al.* (2018) in an analysis of published results related to the effects of the shapes of filler particles on barrier properties of polymer composite films. The collected data from a very large number of studies showed extremely diverse results. However, a few general trends were evident. First, there was no consistent evidence of a positive contribution to tortuosity when using rod-shaped or fibrillar particles. Second, tortuosity was generally found to make a significant contribution to barrier performance when using platy filler particles such as montmorillonite (*i.e.* nanoclay).

Grease-resistant Nanocellulose Films

Because diverse types of nanocellulose and related materials are available, it is important to consider what type to select when the aim is to achieve greaseproof performance. There appears to be a consensus that highly fibrillated cellulose products, *i.e.* micro- and nanofibrillated cellulose (MNFC), hold particular promise on account of their ability to form high-density layers (Aulin *et al.* 2010; Lavoine *et al.* 2012; Sirviö *et al.* 2014). MNFC products are obtained by subjecting cellulose material to very extensive mechanical shearing, often after pretreatment with either enzymes or some form of oxidation to provide carboxylic acid groups on the material. Aulin *et al.* (2010) used carboxymethylation as a means of obtaining MNFC having carboxylic acid groups on the particle surfaces. Such groups, in their dissociated form, provide colloidal stability in aqueous suspension, whereby the repulsion between like-charged surfaces tends to keep the material in a relatively homogeneous dispersion, ultimately resulting in a dense, relatively defect-free film when the material is dried. Figure 6 illustrates the concept of dense layers that can be prepared from cellulose nanofibrils, which combine a high level of nanocrystal content (which are completely impervious to diffusing molecules) and the high flexibility contributed by the non-crystalline cellulose.

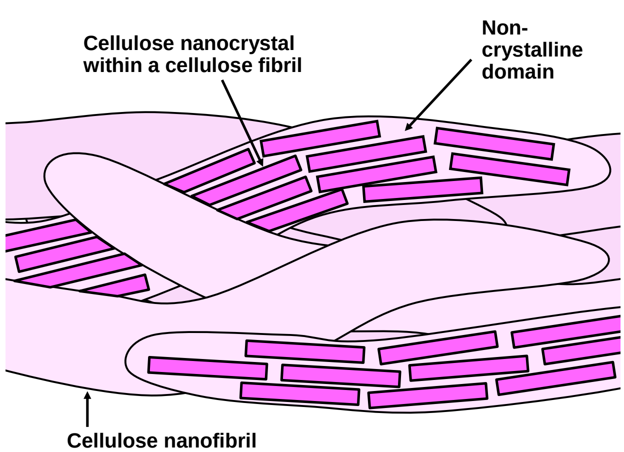


Fig. 6. Schematic illustration of part of the cross-section of a film prepared by the drying of a MNFC aqueous suspension, emphasizing the nanocrystalline zones within such fibrils

As noted by Kumar *et al.* (2014), nearly equivalent performance often can be achieved with the use of microfibrillated cellulose, *i.e.* the same type of material but with a lower degree of size reduction compared to nanofibrillated cellulose. Cellulose nanocrystals (CNC) recently were used in a formulation that achieved resistance to grease (Tyagi *et al.* 2018, 2019), and the results were attributed in part to the high crystalline content of CNC.

Films incorporating montmorillonite

In view of the earlier discussion of tortuosity, it should not be surprising that promising results for resistance to grease and various gases have been achieved in systems in which highly platy minerals were used as an ingredient in film in barrier layers that were mainly comprised of MNFC or CNC (Sanchez-Garcia *et al.* 2010; Liu *et al.* 2011; Aulin *et al.* 2012; Wu *et al.* 2012; Rhim *et al.* 2013; Rastogi and Samyn 2015; Tyagi *et al.* 2018). Though most such studies did not report results for grease resistance, those that did so achieved promising results (Tyagi *et al.* 2018, 2019; Tayeb and Tajvidi 2019).

Hydrophilic polymers

The properties of MNFC films also can be enhanced by the incorporation of various hydrophilic polymers. Examples of such work are as follows (Sirviö *et al.* 2014; Kisonen *et al.* 2015). Notably, Sirviö *et al.* (2014) *et al.* discovered that films prepared with NFC and alginate could be further enhanced by the addition of calcium ions, which appeared to contribute a cross-linking effect among the numerous carboxylate groups.

Hot-pressing

As was noted earlier, nanocellulose-based barrier films can be vulnerable to the effects of high levels of humidity or contact with aqueous solutions. One of the most promising approaches to address such vulnerability was discovered by Österberg *et al.* (2013), who treated the films by hot-pressing. The hot-pressing of the MNFC films was reported to increase in toughness as well as barrier properties. The observed effects were likely due to coalescence among the polymer segments at the cellulose surfaces, with the formation of a denser and more organized system of hydrogen bonding (Pönni *et al.* 2012). The effect might be related to the beneficial effects of calendering of glassine paper, as discussed earlier (Meinander 2000; Kjellgren and Engström 2005). Due to the simplicity and relatively low environmental impact of the procedure, follow-up work is recommended.

Susceptibility to Defects

Even a highly dense cellulosic film with extensive internally-directed hydrogen bonding can be expected to give poor barrier performance if it has pinholes or cracks. For example, Javed *et al.* (2017) found that it was necessary to apply about four layers of a starch-PVOH layer onto glassine paper to overcome effects of defects within individual film layers. Tyagi *et al.* (2018) observed that the incorporation of montmorillonite into CNC-based barrier films resulted in the elimination of defects observable by electron microscopy. It is suggested that related research focused on resistance to grease and oils could be considered in future research.

Due to the high density and crystallinity of typical nanocellulose-based films, it is reasonable to expect problems due to cracking. Kumaki and Kawagoe (2019) recently patented a system to overcome such vulnerability by combining a greaseproof layer with a paper base, to provide structural support. Another promising approach is to use plasticizers such as glycerol in grease-resistant films (Trezza and Vergano 1994; Trezza *et al.* 1998; Park *et al.* 2000; Jansson and Jarnström 2006; Javed *et al.* 2017). Such additives are expected to make nanocellulose-based films more flexible, but with reduced effectiveness in resisting the passage of gases and oils (Hubbe *et al.* 2017b). Also, when selecting plasticizers, health and environmental implications need to be considered (Oehlmann *et al.* 2009). For instance, di-butylphthalate, a widely used plasticizer, has been shows to disrupt the endocrine systems of mammals.

How to Apply Nanocellulose in and on Paper Products

Given that many publications have shown promising effects of nanocellulose with respect to grease resistance, practical means of incorporating these materials into paper products need to be considered. Two main approaches are either by adding MNFC to the slurry of fibers before the paper is formed or by applying MNFC-based formulations to paper's surface.

Internal addition

Technology related to adding MNFC to the fiber slurry before the paper is made, which also can be called wet-end addition or internal addition, has been reviewed (Salas *et al.* 2019). Such studies usually focus on the strength properties of the resulting paper. Barrier properties usually have not been considered in such studies, and it seems likely that a high ratio of ordinary papermaking fibers and MNFC in such sheets might not be a promising approach to achieving grease resistance. This is because, as has been shown by work already discussed in this review, greaseproof performance (in the absence of perfluorochemicals) requires an impermeable barrier, whereas ordinary paper is highly porous. A minor content of MNFC added to ordinary paper furnish would not be able to fill the voids between the fibers. On the other hand, it should be borne in mind that MNFC can be regarded as just a more extreme example of the high levels of refining already being used for the production of glassine paper (Kjellgren and Engström 2005). It would be interesting to find out whether incorporation of different levels of MNFC, along with suitable chemical treatments to enhance retention efficiency and drainage (Rice *et al.* 2018), could provide future options for glassine paper production. There is an inherent challenge to such efforts, since drainage enhancement requires the water to flow more rapidly through the paper during its preparation, whereas the end goal is to slow down or stop the flow of another fluid (grease) in the dry paper. Success is likely to depend on the effectiveness of wet-pressing, drying, and calendering operations in closing up the pore spaces between fibers in the paper.

Surface application

Surface application systems that are widely used in papermaking include size-press and coating procedures. Such application processes have been employed to evaluate the effects of MNFC applied to paper surfaces (Aulin and Ström 2013; Lavoine *et al.* 2014; Vartianen *et al.* 2016; Hubbe *et al.* 2017a). Besides, spray application has been used to form MNFC layers onto paper (Beneventi *et al.* 2014, 2015; Shanmugam *et al.* 2017, 2018; Mirmehdi *et al.* 2018). The rheology of nanocellulose suspensions, which has been recently reviewed (Hubbe *et al.* 2017b), can be expected to place constraints on the speeds and amounts of MNFC that can be applied in different situations.

Water removal is another issue that places serious constraints on the scale-up of MNFC surface application technologies to industrial scale. That is because such surface layers cannot be expected to be stable until water has been removed. Suspensions of MNFC have to be quite dilute to achieve sufficiently low viscosity in order to be used in practical coating operations (Hubbe *et al*. 2017b). In this regard, applying an aqueous mixture with MNFC to the surface of a paper web can offer an important advantage. In addition to the evaporation of water from the film, much of the water also can be wicked into the paper web by capillary action (Hubbe *et al*. 2017a). Such wicking, combined with the fact that only a thin layer might be required in order to achieve the needed barrier properties, has the potential of speeding up the immobilization of the surface layer, making it possible to achieve commercially viable rates of production.

Layers

Multi-layer systems at the nanoscale can be used to achieve different combinations of needed properties (Hammond 2004). A two-layer approach was employed recently by Tyagi *et al*. (2019) to achieve a combination of grease resistance and tolerance of humid or wet conditions. First, the grease resistance was achieved by use of an MNFC layer. Second, a protective, water-resistant layer was prepared with a combination of CNC, montmorillonite clay, and protein. CNC was selected for the water-repellent layer due to its very high crystallinity, which can be expected to reduce its sensitivity to water. Earlier work by the same group showed that alkylketene dimer (AKD) also can be used in such formulations with CNC to increase resistance to water (Tyagi *et al*. 2018). Figure 7 is a schematic diagram that incorporates features from the two last-cited articles. A benefit of the described technologies is that they make it possible to protect a greaseproof layer from moisture without resorting to plastic lamination. Preferably, the entire coated paper product is formulated in a manner that would be suitable for paper recycling. Some technical requirements to consider when developing this kind of system, in addition to grease resistance, may include crack resistance, gas permeability, hydrophobicity (water contact angle), and resistance to water vapor permeation.

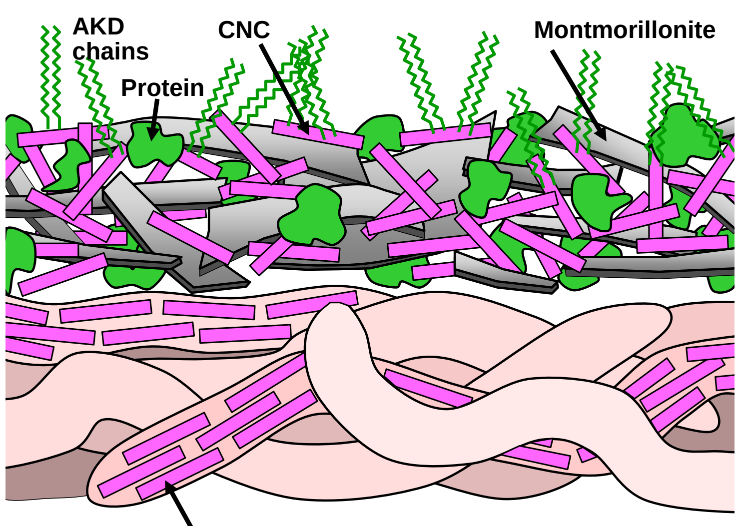


Fig. 7. Schematic illustration of a two-layer system by which nanocellulose-rich layers are used to achieve grease resistance (due to an MNFC layer) and protection of that layer using a water-resistant layer (with CNC, montmorillonite, protein, and reacted alkylketene dimer)

CLOSING COMMENTS

As shown in the studies considered in this review, there are numerous viable options available for potential future commercial developments in the area of greaseproof paper products. Options span the range from improvements in fluorochemical-related technologies, to parchmentization by immersing the paper into concentrated sulfuric acid, to glassine paper made by high levels of refining, and the recently emerging field of nanocellulose-rich film applications to achieve grease barrier performance. The future of such ventures depends not only on research progress but also on potential changes in regulations and business practices with respect to the usage of fluorochemicals. It seems unlikely that industrial production facilities will be fully ready to cope with or take advantage of any abrupt new restrictions in the usage of fluorochemicals in food-contact applications. Also, there is a continuing need to enhance the performance of perfluorinated additives for paper treatment. Issues of concern include the efficiency of retention of the agents during the formation of paper, and improving the relationship between cost and performance. In any case, the field of grease-resistant products based on paper seems to be a promising field for further research in the coming years.

ACKNOWLEDGEMENTS

The authors are grateful to the following people who checked an earlier draft of this document and provided their feedback: Henrik Kjellgren, Nordic Paper Seffle AB, SE-66129 Säffle, Sweden; Camille Brule, North Carolina State University; Stuart Lang, Huhtamaki Inc., Albertville; and Caryn Peksa, Daikin America.

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