

Self-assembly of Alkyl Chains of Fatty Acids in Papermaking Systems: A Review of Related Pitch Issues, Hydrophobic Sizing, and pH Effects

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This review article considers the role of fatty acids and the mutual association of their long-chain (e.g. C18) alkyl and alkenyl groups in some important aspects of papermaking. In particular, published findings suggest that interactions involving fatty acids present as condensed monolayer films can play a controlling role in pitch deposition problems. Self-association among the tails of fatty acids and their soaps also helps to explain some puzzling aspects of hydrophobic sizing of paper. When fatty acids and their soaps are present as monolayers in papermaking systems, the pH values associated with their dissociation, *i.e.* their pK_a values, tend to be strongly shifted. Mutual association also appears to favor non-equilibrium multilayer structures that are tacky and insoluble, possibly serving as a nucleus for deposition of wood extractives, such, as resins and triglyceride fats, in pulp and paper systems.

Keywords: Wood extractives; Hydrophobic effect; Papermaking; Pitch deposits; Sizing of paper

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INTRODUCTION

Importance of the Topic

The extractives component of wood material, which includes various fatty acids and their esters, has long presented a series of challenges to the pulp and paper industry, including outbreaks of pitch deposition and effects related to the hydrophilic or hydrophobic character of the resulting paper. Though the wood extractives comprise only about 1 to 5% of the dry mass of hardwood and 3 to 8% of that of softwood (Biermann 1996), they are usually a nuisance, but sometimes also of value, as in the case of rosin products and turpentine. Previous reviews of these extractives and their effects mainly have emphasized effects due to components and topics other than the fatty acids; for instance, the resin acids often comprise a more major fraction of material found in pitch-like deposits in paper machine systems (Allen 2000b; Back 2000). Also, the resin acids are well known to impart water-resistance to paper, *i.e.* to confer “rosin sizing” (Vandenberg and Spurlin 1967). This review article considers a hypothesis that the fatty acids and their esters – and specifically the tendency of mutual association of the alkyl chains of the fatty acids – often play a highly influential role in the behavior of extractive materials present within papermaking systems. A better understanding of these relationships has the potential to contribute to progress in the following areas:

- Prediction of conditions leading to deposition of wood-derived hydrophobic compounds in paper machine systems
- Development of new and improved pitch-control measures and related chemical additives and processes
- Developments in paper sizing technology that make use of fatty acids, a group of highly available, inexpensive, and relatively environmentally friendly compounds
- Progress in understanding some puzzling aspects related to the behavior of paper machine systems in which fatty acids, their soaps, and their esters are present in significant amounts

This article is organized around the following central observation: It has been found that fatty acid compounds, including oleic, stearic, and palmitic acids, *etc.*, dissociate at a much higher pH compared to analogous compounds that do not have long alkyl ($\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-}$ *etc.*) tails (Nyrén and Back 1958a,b; McLean *et al.* 2005a; Strand 2013; Pashkovskaya *et al.* 2018). The fatty acids naturally present in wood materials tend to be dominated by 16-carbon or 18-carbon chain length and either one, two, or three C=C double bonds (Vercoe *et al.* 2004). The dissociation of such fatty acids is often suppressed until the pH is raised two or three units higher than such compounds as acetic acid, especially at a relatively low ionic strength of solution (McLean *et al.* 2005a). This review article will consider various reported evidence suggesting that the mechanisms underlying this effect, called the “colloidal $\text{p}K_a$ ”, may help in the understanding of a variety of other hard-to-explain phenomena in papermaking systems.

Hypotheses

The following hypotheses will be considered in this article as a means of focusing attention on the role of mutual association of relatively long alkyl chains (say with more than 14 CH_2 groups) in pulp and paper operations and some other systems:

1. It is proposed that certain distinctive behavior of wood extractives in papermaking systems, as a function of pH, can be better explained when taking into account a tendency of mutual association of long-chain alkyl (or alkenyl) groups.
2. It is proposed that certain effects of pH on the tendency of wood extractives to form deposits can be explained by the colloidal pK_a concept.
3. It is proposed that the relative lack of progress, up to this point, in development of hydrophobic sizing systems for paper based on fatty acids and their soaps can be explained by the colloidal pK_a concept and the close packing of the alkyl (or alkenyl) chains.
4. It is proposed that the mutual association of alkyl (or alkenyl) chains also can help to explain the effectiveness of certain alkaline or “reactive” sizing systems, such as those involving the use of alkylketene dimer (AKD) and alkenylsuccinic anhydride (ASA)

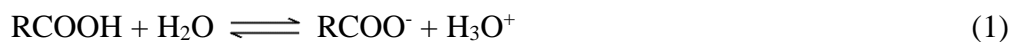
To address these hypotheses, in the light of published articles, the first step will be to review some theoretical concepts. Also, various evidence to support such concepts will be reviewed. The concepts include theories of the dissociation of carboxylic acids, factors that affect the pH at which half of those groups are dissociated (*i.e.* the pK_a), the formation of monomolecular layers of fatty acids and their soaps at interfaces, a concept called “colloidal pK_a ,” and a variety of competing effects that can be expected to obscure or add to effects that can be attributed to fatty acids. The next point of focus will be possible ways in which the tendency of mutual association of fatty acid alkyl chains can affect pitch-control strategies, hydrophobic sizing of paper, and some broader applications, such as adhesion to surfaces, soil wettability, and superhydrophobicity in systems where fatty acids and their soaps are present.

This document builds upon progress achieved by others. Such progress has been summarized in review articles and monographs, which deal in a broad way with pitch deposition and hydrophobic sizing effects in pulp and paper mill systems (Allen 1980, 2000a,b; Back 2000; Hubbe *et al.* 2006; McLean 2008; Tanase-Opedal *et al.* 2011a). Analytical procedures to quantify wood resins in papermaking processes were reviewed by Valto *et al.* (2012).

THEORETICAL CONCEPTS

Dissociation of Weak Acids and the pK_a Value

Because the main points to be considered in this review article involve the pH of dissociation of different carboxylic acid groups, some basics will be summarized here. When a pure carboxylic acid is placed in water, the pH value will determine the state of ionization. The equilibrium expression, for each class of carboxylic acid group, can be described by Eq. 1.



When the net concentration and other parameters such as temperature are known, the extent of dissociation ordinarily can be obtained by use of published values of acid dissociation constants, which are generally defined for each type of carboxylic acid according to Eq. 2:

$$K_a = [\text{RCOO}^-] * [\text{H}_3\text{O}^+] / [\text{RCOOH}] \quad (2)$$

Analogous to the definition of pH, the pK_a is defined as the negative logarithm (base 10) of the K_a value, as in Eq. 3:

$$pK_a = -\log K_a \quad (3)$$

To illustrate the practical effects of these relationships, Fig. 1 shows how the dissociation of a simple carboxylic acid, acetic acid, changes its form in aqueous solution depending on the pH. As shown in the figure, the dissociation does not take place all at once. Rather, about 90% of the transition from the uncharged to the fully charged state, within a population of such groups, will happen within a span of two units of pH. The pK_a value is in the center of this range, where 50% of the groups are ionized. The plotted line is based on Eq. 4:

$$\text{Fraction ionized} = 1 / [1 + (10^{-\text{pH}} / 10^{-pK_a})] \quad (4)$$

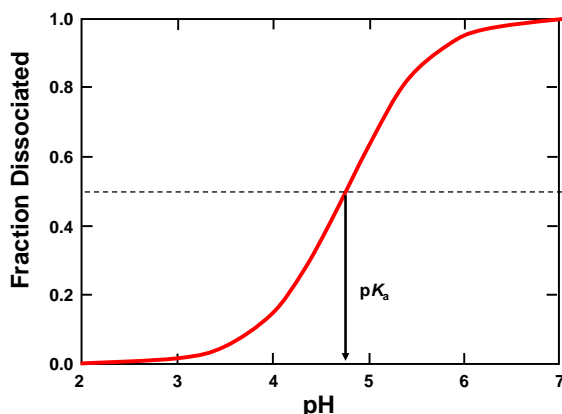


Fig. 1. Dissociation of aqueous acetic acid as a function of pH. Curve calculated based on a pK_a value of 4.757, as reported by Mesmer (1989)

Evaluation of the pK_a values of fatty acids having chain lengths above about 14 can be challenging, partly due to their relatively low solubility in water, especially in their uncharged state. One of the earliest strategies to get around this problem has been to employ a water-alcohol mixture as a solvent. By using a mixture of water and ethanol, White (1950) estimated the pK_a values of palmitic and oleic acids, respectively, to be 5.06 and 5.02. Earlier work, using related methods, obtained pK_a values in the range 4.9 to 5.0 for lauric, palmitic, stearic, and oleic acids (Jukes and Schmidt 1935). All of these values are near to the values for acetic acid (4.76, see Mesmer *et al.* 1989), which is typical for monocarboxylic acid species that are highly soluble in water. Sue *et al.* (2004) obtained similar pK_a values (near 4.8) for aqueous solutions of n-alkyl carboxylic acids with relatively short chain lengths between one and six.

Back and Steenberg (1950) developed methodology for determination of the pK_a values of wood extractive compounds, including fatty acids having alkyl or alkenyl chain lengths as high as 18. They found that such determinations could be carried out in aqueous solution by starting at a sufficiently high pH such that the compound to be analyzed is

essentially 100% in its ionic form, *i.e.* a carboxylate salt. By titrating such solutions with strong acid, they determined the pK_a value of abietic acid to be 7.6.

Effects of adjacent ionically charged groups on pK_a

The pK_a value of a carboxylic acid group will be shifted by the presence in the same compound of electron-withdrawing or electron-contributing atoms and groups, *i.e.* contrasting electronegativity of the neighboring atoms in the compound (Zhang *et al.* 2006). Such an effect can explain the relatively low pK_a values (about 3.3) of carboxylic acids that are attached at an alpha position relative to an oxygen (*e.g.* uronic acid), which are abundant in certain hemicelluloses and their products of decomposition after pulping and bleaching (Laine *et al.* 1996).

Multi-carboxylic Monomeric Acids

When the compound under consideration contains other ionically charged groups, in addition to the carboxylic acid under consideration, then the neighboring group influences can be relatively large. Because such effects play a critical role in the systems to be considered in this article, some key concepts will be illustrated by using citric acid as an example.

The structure of a citric acid molecule is shown in Fig. 2. Also shown is an example of successive dissociation steps, eventually leading to a fully dissociated molecule with three negative charges. Table 1 documents results of several studies that have evaluated the pK_a values for these dissociation steps. The slight differences between results obtained in different studies can reasonably be attributed to such factors as (a) advances in the quality of available instruments with the passage of time, (b) effects due to dissolved carbon dioxide from the air, and (c) calibration issues.

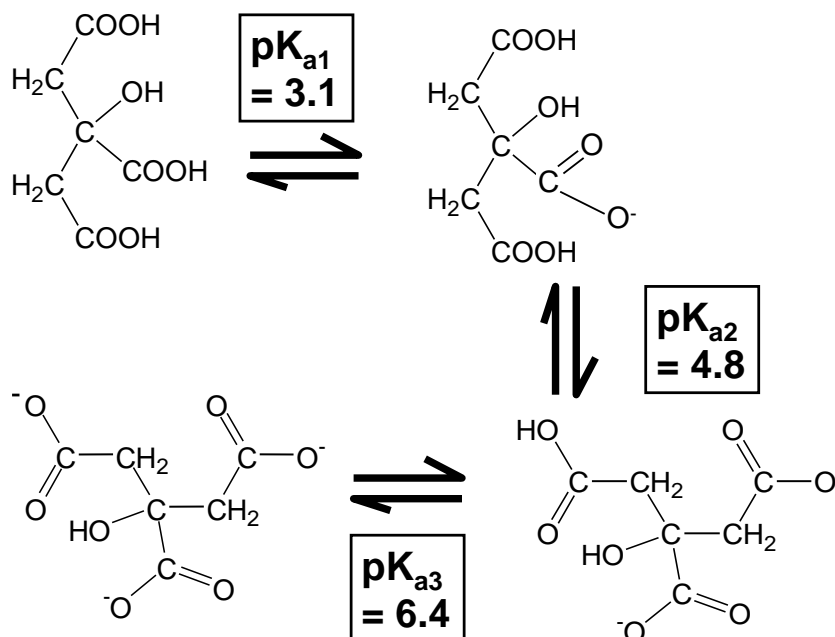


Fig. 2. Chemical structure and an example of successive dissociation steps of citric acid

Table 1. Reported pK_a Values for the Three Dissociation Steps of Citric Acid

Salt	$pK_a(1)$	$pK_a(2)$	$pK_a(3)$	References
None	3.08	4.39	5.49	Hastings & Van Slyke 1922
None	3.15	4.77	6.40	Bates & Pinching 1949
None	3.11	4.44	5.83	Saeeduddin <i>et al.</i> 1996
None	3.13	4.76	6.40	Bénézeth <i>et al.</i> 1997
None	3.13	4.76	6.40	Crea <i>et al.</i> 2004
0.1 M NaCl	2.90	4.34	5.68	Bénézeth <i>et al.</i> 1997
0.1 M NaCl	2.92	4.35	5.77	Crea <i>et al.</i> 2004
1.0 M NaCl	2.79	4.08	5.28	Crea <i>et al.</i> 2004
5.0 M NaCl	3.06	4.40	5.29	Crea <i>et al.</i> 2004
Sat. NaCl	2.28	4.32	5.41	Bénézeth <i>et al.</i> 1997

As shown in the table, each successive dissociation step for citric acid requires an increase of about 1.3 pH units above the preceding pK_a value in order to bring about dissociation of 50% of the next carboxylic acid. The second dissociation is different from the first because one of the carboxylic acid groups is already ionized, and the presence of the ionic charge tends to suppress the dissociation of the next group. Likewise, the presence of two ionized groups nearby on the molecule further suppresses the third dissociation.

It is also apparent from Table 1 that salt addition generally decreased the observed values of pK_a . This can be attributed to a shielding effect of the salt ions (Stigter 1991; Hunter 2001). It is well known that salt ions in solution, depending on their concentration, decrease the Debye-Hückel length parameter, κ^{-1} , which is related to the thickness of ionic double layer effects in solution and at surfaces (Hunter 2001). Strong interactions between adjacent ionizable groups can be anticipated when they are close together relative to the value of κ^{-1} .

Polymeric Carboxylic Acids

Polymers having a multiplicity of carboxylic acid groups provide further useful examples from which to understand the effects of neighboring groups on the equilibria of dissociation. Publications have shown that the dissociation of carboxylic acid groups within polycarboxylic acid materials tends to be suppressed relative to similar separate, monomeric groups, especially in the absence of salts (Ghosh 1976; Bradna *et al.* 1994; Lutzenkirchen *et al.* 2011). With increasing salt concentration, the difference is less, which provides another example of the screening of the electrostatic effects by the ions in solution (Bradna *et al.* 1994; Lutzenkirchen *et al.* 2011). Panagiotopoulos (2009) showed that such data also can be fitted using a numerical simulation approach.

Related evidence has been found when studying the surface charges of cellulosic pulp fibers. Detailed work by Herrington and Petzold (1992a,b) showed that the dissociation of carboxylic acid groups at cellulosic fiber surfaces tends to be spread out over a wider range of pH than can be attributed to a single acid dissociation process, as would be represented by Eq. 4. Figure 3 compares curves reported by Herrington and Petzold (1992a) to a calculated curve for acetic acid (Mesmer *et al.* 1989). Since the carboxylic acid groups associated with kraft pulp fibers are mainly of one general type (Laine *et al.* 1996), the best explanation is that dissociation of one selected group suppresses the dissociation of similar nearby groups along the chain.

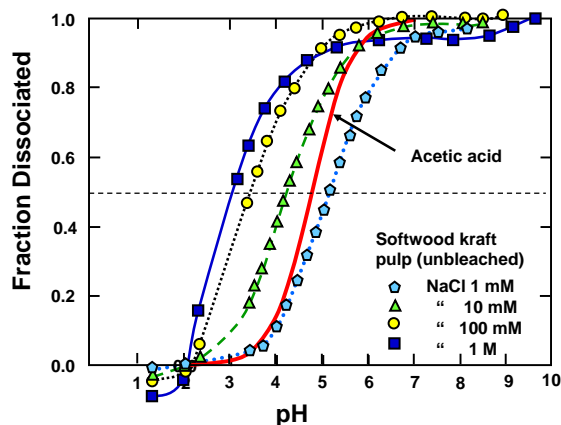


Fig. 3. Comparison of potentiometric titration curves obtained for cellulosic fiber suspensions, at different salt concentrations (Herrington and Petzold 1992a), with calculated results for acetic acid. Negative values correspond to surfaces having a net positive charge, consistent with protonation of other functional groups.

Bygrave and Englezos (1998) showed that the fitting of potentiometric titration data could be improved by simultaneous use of more than one value of pK_a . These authors were implicitly assuming that dissociation of some groups at the fiber surfaces makes it more difficult to dissociate subsequent carboxylic acid groups in the near vicinity. It is also worth noting that ordinary high-yield papermaking pulps will contain not only hemicellulose-type COOH groups, but also the carboxylic acids groups associated with any residual fatty acids and resin acids. The latter will generally have higher pK_a values than the hemicellulose-type groups for two reasons. First, there are no oxygen atoms at adjacent carbons in the extractive compounds. The second reason, to be discussed in a subsequent section, is called the colloidal pK_a effect.

The salt effects shown in Fig. 3 (Herrington and Petzold 1992a) are consistent with a shielding effect, which can be expected to be especially effective in cases where the ionizable groups are farther apart than when attached to adjacent carbons in a polymer chain. Budd and Herrington (1989) reported that increasing salt is able to shift the apparent pK_a values of carboxylic acid groups at fiber surfaces by about two pH units toward lower values. It is well known that shielding effects become much greater as the distance becomes larger than κ^{-1} , the effective thickness of an electrical double layer in the system (Hunter 2001).

Monolayers of Fatty Acids and their Soaps

The science of the spreading of oleophilic films got its start with a publication by Benjamin Franklin, who spread a teaspoonful of olive oil on Derwent Lake in England, with a dramatic demonstration of the stilling of waves (Franklin *et al.* 1774; Binks 1991). Major breakthroughs in the field were achieved by Langmuir (1917), who was the first to demonstrate that compressed fatty acid monolayers occupy approximately the same area per molecule, independent of chain length.

Though the achievements of Langmuir continue to be greatly respected, subsequent researchers have quantified significant differences in the stability of monolayers of fatty acids and their salts, depending on such factors as chain length. Some key findings are summarized in Table 2.

Table 2. Work Related to the Stability of Monolayer Films of Fatty Acids and their Salts as Affected by Alkyl or Alkenyl Chain Length

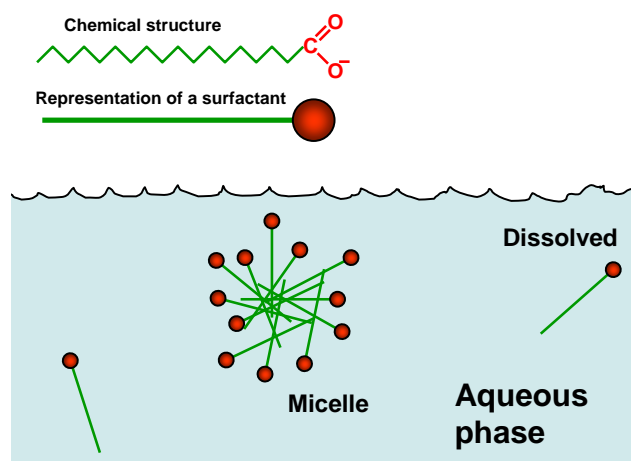
Observation	References
Stable films formed when chain length (n) > 11.	Allara & Nuzzo 1985
Fatty acid salts in Cu with n > 8 were hydrophobic.	Ein-Eli 2008
Alkylthiols become stable when n > 15.	Broniatowski 2009

As noted by Vollardt and Fainerman (2006), a compressed monolayer may contain more than one type of ordered phase, even when just one type of surface-active molecule is present. Phases and phase transitions involving condensed monolayers at interfaces have been reviewed (Kaganer *et al.* 1999).

When an insoluble monolayer at the water surface is subjected to sufficient pressure, within the plane of the layer, it will undergo collapse. Joos (1971) studied the relationship between pH and collapse pressure. Lee (2008) reviewed evidence pertaining to such collapse and concluded that it typically involves a folding mechanism. Vaknin *et al.* (2007) showed that folding and collapse can lead to stable bilayer and trilayer structures. Details of the layer structures were different in the presence or absence of cationic ions in the aqueous phase.

Micellization

When surface-active molecules are placed in water, one ordinarily can expect a tendency of mutual association (Zana 1996, 1997). Whenever the concentration in aqueous solution is above a level called the critical micelle concentration (CMC), the mixture will contain micelles, *i.e.* groups of about 7 to 64 surfactant molecules with the headgroups near the interface of the aqueous phase and with tail groups self-associating in a disorganized pattern (Zana 1997). As illustrated in Fig. 4, within each micelle the surfactant molecules will have a preferential association in which the hydrophobic tails are gathered into a predominantly hydrophobic region.

**Fig. 4.** Schematic description of a micelle, in which surface-active molecules are depicted as a hydrophilic headgroup and a hydrophobic tail

The hydrophilic headgroups generally will be directed outwards from each micelle towards the aqueous phase. Though forces of interaction favor the growth and regular organization of the micelles, thermal forces continually act to randomize the system.

Though Fig. 4, for simplicity, represents the tail groups as straight sticks, molecular dynamic simulation studies predict that they will have a wide variety of randomized conformations at any moment (Zana 1997).

The CMC value corresponding to a given type of surface-active compound can be used as an indicator of the strength of mutual association among the surfactant molecules in a mixture. Thus, studies have shown a strong decreasing tendency of CMC with increasing alkyl or alkenyl chain length (Ström 2000; Brito *et al.* 2011; Kroflic *et al.* 2011). This makes sense because the free energy of mutual association increases in proportion with the chain length (Tanford 1980). Zana (1996) reviewed related literature and estimated that mutual association among dodecyl chains in a monolayer structure contributes approximately -20 kJ/mole of free energy.

If there is unsaturation (*i.e.* a C=C double bond) in the tail, the effect is to make the tail act as if it were about two carbons shorter, relative to the CMC expected for the fully saturated analogue (Brito *et al.* 2011). This makes intuitive sense based on the average shape of the molecule. A double bond, especially if it is of the *cis* type, will cause a persistent bend, which will decrease the average end-to-end length of the chain.

Several researchers have shown that the CMC of ionically charged surfactants tends to decrease with increasing ionic strength (Lin *et al.* 2005; Šarac and Bešter-Rogač 2009; Kroflic *et al.* 2011; Kakehashi *et al.* 2012). The explanation for such effects again appears to involve a shielding effect. Shielding of the electrostatic forces due to the presence of salt will reduce the importance of the ionic charges with respect to solubility of the compound.

Self-assembly at Interfaces

The term self-assembly indicates systems in which molecular components become organized in a regular, seemingly planned manner, but without the need for external control. This term becomes relevant in the case of fatty acids and their salts when one considers how they organize themselves at interfaces, in micelles, and in bubbles. Allara and Nuzzo (1985) as well as Touwslager and Sondag (1994) showed that long-chain alkanolic acids can form close-packed oriented monolayers on oxidized alumina surfaces. Touwslager and Sondag (1994) found that the degree of order within such self-assembled layers increased with increasing chain length. In other words, longer alkyl chains provided a greater tendency for self-association and ultimately tighter and more perfect monolayer films. Liascukiene *et al.* (2014) proposed that self-association was the key mechanism by which fatty acid addition to water in the presence of oxidized aluminum rendered such surfaces hydrophobic. Sobhana *et al.* (2017) recently found evidence of self-association when cellulose fibers were first treated with silver-aluminum double hydroxides, followed by addition of stearic acid a pH of about 10, which is sufficient to keep the compound in its soap form. Again, the resulting hydrophobic effect was attributed to self-association of the fatty acid soap molecules onto the cationic treated surfaces, forming a well-ordered monolayer with the water-hating tails pointing outwards. It has been shown that when aluminum species have been formed on the surface of pulp fibers, thus constituting a mordant, various fatty acids can then arrange themselves in a layer to provide effective hydrophobic sizing (Shimada *et al.* 1997).

Considerable progress has been achieved in characterizing the tightness of packing within long-chain alkyl and alkenyl chains at interfaces. Findings are summarized in Table 3, along with some selected references. As shown, double bonds within the hydrophobic chain, especially those with *cis* conformation, tend to resist the tight packing of the monolayers. When the surfactant molecules have charged headgroups, such as carboxylate,

this tends to expand the monolayer film, but such effects are opposed if the solution contains divalent cations such as calcium or magnesium ions. The situation with aluminum ions is more complex (Binks 1991), which is consistent with the dominance of different aluminum ionic species as a function of pH (Bottero and Fiessinger 1989; Bi *et al.* 2004).

Table 3. Factors Affecting the Tightness of Packing of Long-chain Fatty Acid and Related Monolayers

Key Factor	Observation	References
Chain length	Increasing density with increasing chain length. The orientation of fatty acid chains became perpendicular to the interface at high chain length.	Tao 1993; Touwslager & Sondag 1994
Unsaturation	Decreasing density due to C=C double bonds in the chain.	Langmuir 1917; Polimeno <i>et al.</i> 2001; Kanicky and Shah 2002; Vollhardt & Fainerman 2006; Vollhardt 2007; Sundberg <i>et al.</i> 2009; Strand 2013
Headgroup repulsions	Headgroup repulsions (especially electrostatic) decrease the density.	Adam 1921; Adam & Miller 1933; Binks 1991; Johann <i>et al.</i> 2001; Polimeno <i>et al.</i> 2001
Multivalent cations	Dense films, especially with Ca ²⁺ , but sometimes expanded with Al ³⁺ .	Goddard and Ackill 1963; Binks 1991

Fatty acids within natural samples of wood and related bioresources are invariably mixtures, containing a range of unsaturated (such as oleic, linoleic, and linolenic acids) and saturated (such as stearic acid) components, in addition to triglyceride fats and other hydrophobic compounds such as β -sitosterol (pine oil). Studies have shown that when such mixtures are collected as monolayer films, some of the component compounds may become self-segregated into separate domains (Angelova *et al.* 1994; Lieckfeldt *et al.* 1994; Johann *et al.* 2001; Ocko *et al.* 2002; Torrent-Burgués 2018).

Free Energy of Association

To account for the aforementioned effects, including micellization, the tightness of packing, and segregation of different compounds within spread monolayers, there has been progress with respect to determining the free energy of interaction associated with monolayers of fatty acids, their salts, and related compounds.

Wang *et al.* (2011) determined values of free energy in the range 30 to 40 kJ per mole of surfactant molecules, for their mutual association in micelles. Earlier, Boyd (1958) calculated the free energy of transfer from a melted fatty acid phase to a spread monolayer to be approximately 20.92 kJ per mole in the case of palmitic acid at room temperature. The latter value is smaller than it might be, since it does not consider a hypothetical (but unrealistic) initial state at which the molecules are individually dissolved in the aqueous solution.

It is tempting, but also potentially misleading, to attribute the free energy of association among alkyl or alkenyl chains in a monolayer to just the van der Waals components of forces (see, for instance, Wellen *et al.* 2017). Since the alkyl (or alkenyl) chains are nonpolar, the tendency of mutual association has been called “hydrophobic effect.” There is no denying that the dispersion force (London) components of van der Waals forces act between adjacent molecules, whether charged or uncharged, polar or

nonpolar. However, according to Tanford (1980), in fact the largest contribution to the hydrophobic effect, including the energy of association of alkyl chains, consists of hydrogen bonding. This is because the free energy of the system is minimized when hydrophobic substances are segregated, allowing more of the water molecules to be completely associated with each other, for which hydrogen bonding contributes the largest contribution of free energy. Attraction between the tails themselves is not the dominant influence. Meyer *et al.* (2006), reviewed experimental evidence indicating that, regardless of its origins, the hydrophobic effect is short in range (< 10 nm).

Colloidal pK_a

The term “colloidal pK_a ” refers to the observation that the dissociation constants of long-chain fatty acids take on different values when the molecules are associated together, especially in the absence of salt ions. This effect was apparent already in the results reported by Nyrén and Back (1958a). They reported that the pK_a of lauric (C12) and myristic (C14) acids was markedly different depending on whether the determination was carried out at low concentration or high concentration of the respective fatty acids. As shown in Table 4, the pK_a values were observed to increase by between 1.2 and 1.7 pH units when increasing the concentration, thereby allowing micelles to form and govern the behavior of most of the fatty acid molecules present.

Table 4. Effects of Low vs. High Concentration of Fatty Acid on the pK_a Values of Lauric and Myristic Acids

Type of Fatty Acid	Lauric	Myristic
pK_a at low concentration	5.3	6.3
pK_a at high concentration	ca. 7	ca. 7.5

Data from Nyrén and Back (1958a)

Reported findings regarding colloidal pK_a are listed in Table 5. The reported findings can be summarized as follows: The state of dissociation of the carboxylic acid groups is greatly influenced by their being held in very close proximity to each other. Thus, the observed shifts in pK_a tend to be the greatest in the case of stearic acid (C18) or even longer fully saturated alkyl chains (McLean *et al.* 2005a; Strand 2013). Apparently 18 carbons provides sufficient free energy of interaction to overcome such factors as repulsion between the headgroups, which otherwise would tend to expand the monolayer film. As in the case of citric acid, as discussed earlier, the presence of a dissociated, and thereby charged group, will suppress the dissociation of neighboring groups, especially when they are held in such close proximity.

Results resembling a mirror image of those listed in Table 5 were reported by Matulis and Bloomfield (2001a,b), who studied long-chain aliphatic amines. Longer chains and increased concentrations both resulted in lower pK_a values. Each additional methylene group resulted in a further shift of 0.6 to 0.8 pH units of the pK_a . The fact that the shift was in the opposite direction from those considered in Table 5 is consistent with the opposite sign of charge, compared to the examples considered in the table, all of which involved carboxylic acids. Related work by Perger and Bešter-Rogač (2007) showed that micellization of such compounds is favored by higher chain length and by less hydrated counter-ions.

Table 5. Reports of Distinctively High pK_a Values for Close-packed Monolayers of Fatty Acids

Variables tested	Key Findings	References
Concentration of the fatty acid	The pK_a of lauric acid was shifted upwards by about 1.7 units with increasing concentration, consistent with a change from individually dissolved molecules to predominantly micelles in the mixture.	Nyrén and Back 1958a
Location at interface	Ionizable compounds tend to be less ionized when present at interfaces (review article).	Binks 1991
	The pK_a values of carboxyl groups in a packed monolayer were at least one pH unit higher than when present in the bulk of solution.	Dhathathreyan 2008
Chain length	The apparent pK_a values of medium chain fatty acids was about 6, and this rose to about 8 for a higher ratio of oleic acid (having a longer chain length).	Lieckfeldt <i>et al.</i> 1995
	The value of pK_a increased from 6.5 to ca. 9 with increasing chain length of fatty acids from 8 to 16.	Kanicky <i>et al.</i> 2000
	The apparent pK_a increased with increasing chain length, eventually reaching a plateau at pH 9 to 10 for 18 carbons in the absence of salt.	McLean <i>et al.</i> 2005a
	Beyond a chain length of 18, no further increase in pK_a of fatty acids (in micellar solution) was observed. The results were changed when resin acids and triglycerides were also present.	Strand 2013
Chain length, salt and unsaturation	The value of pK_a increased with increasing chain length but fell with unsaturation. Salt addition resulted in higher pK_a .	Sundberg <i>et al.</i> 2009
Double bonds and chain length	For C18 fatty acids, the pK_a decreased from 6.9 (saturated) to 6.45 (one double bond) to 6.1 (three double bonds) in the presence of 20 mM NaSO ₄ . The authors also showed effects of chain length, agreeing with others.	Pashkovskaya <i>et al.</i> 2018
Pure soap addition to water	When adding pure sodium myristate (C12) to water, the pH rose, consistent with protonation of about 1% of the compound. This is consistent with a tendency of charge to be suppressed as a consequence of micelle formation.	Wen & Franses 2000
Salt concentration	The pH was found to rise upon addition of salt to a dispersion of spruce wood components. This is consistent with deprotonation of fatty acids or other species due to stabilization of the ionic forms as a result of shielding effects.	Örså <i>et al.</i> 1997; MacNeil <i>et al.</i> 2011
Salt addition	Addition of small amounts of salt reduced the colloidal pK_a effect. Lower values of pK_a were obtained in the presence of salt, consistent with a reduced influence of adjacent charged groups.	Wellen <i>et al.</i> 2017

Multi-valent Counter-ion Effects

As shown in Fig. 5, the presence of multivalent ions in aqueous solution has been shown to have profound effects on the state of dissociation of carboxyl groups of stearic acid (Aveyard *et al.* 1990; Binks 1991). When evaluated at a concentration of 0.1 mM, the aluminum ions had the greatest effect in decreasing the effective value of pK_a to about 3.5. Although the trivalent aluminum ion (Al^{3+} or more formally as $Al(H_2O)_6^{3+}$) is dominant in

highly acidic solutions, one can expect oligomeric aluminum species, sometimes having a very high valence of +7, to predominate at somewhat higher pH values (Bottero and Fiessinger 1989; Bi *et al.* 2004). A very high strength of complexation of such a multi-valent cationic species with the carboxylate groups is consistent with stabilization of the carboxylate form at exceptionally low pH. Indeed, aluminum has been found to complex strongly with the OH^- ion (Guan *et al.* 2007). Thorium ions in solution have a valence of +4, which explains their high ability to decrease the value of pK_a , as shown in Fig. 5. Calcium ions, with a positive valence of 2, decreased the pK_a by about three pH units compared to a salt-free system (shown at the far right in Fig. 5). Sodium chloride, which was evaluated at a much higher concentration than the other compounds, also decreased the pK_a value in comparison to the salt-free system. These results have high relevance to papermaking systems, in light of the very common usage of aluminum sulfate and related additives during papermaking (Strazdins 1989a). The high valence of the oligomeric aluminum species interacting with the densely packed charged head-groups of fatty acid soap suggests a strong and relatively irreversible complexation (Kubicki *et al.* 1999).

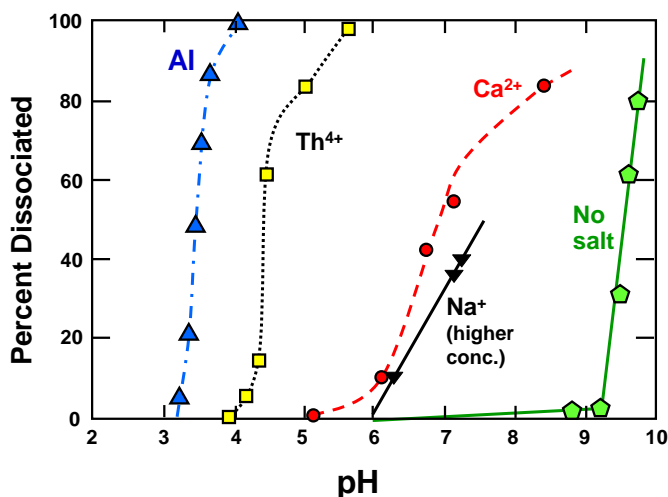


Fig. 5. Effects of the presence of different cations in aqueous solution on the dissociation of carboxylic acid groups of stearic acid in spread monolayer films (figure redrawn from Aveyard *et al.* 1990)

Dimerization of carboxylic acids (pre-micellization and head-to-head)

There are three modes by which fatty acid moieties have been proposed to form stable pairs (Kanicky and Shah 2003; Vercoe *et al.* 2004). It appears that one such mode, if formed, is likely to have an effect on the pK_a values of fatty acids. The other two modes, which can be called, respectively “pre-micellization” and “head-to-head pairing by means of hydrogen bonds,” will be described next, and they are illustrated in Parts A and B of Fig. 6.

As illustrated in Part A of Fig. 6, it is logical to expect that pairs of fatty acid soap molecules, in aqueous solution well above the pK_a value, might tend to pair up with their head-groups facing in opposite directions. That way, the repulsion between the negative charges would be minimized, since the charged headgroups would be relatively far apart. A structure such as that shown in Part A might be hypothesized as an initial meta-stable step leading to the formation of a micelle. Though the structure makes logical sense, there

does not appear to be firm evidence regarding whether, and under what conditions, there are quantifiable amounts of such species present in aqueous systems.

The second mode of dimerization involves a pair of protonated carboxyl species (see Part B of Fig. 6) (Vercoe *et al.* 2004). Such pairing could be expected to play a significant role when the protonated form of carboxylic acid is dissolved in a nonpolar solvent. In such situations, the hydrogen bonding ability of carboxylic acid groups, especially when arranged as shown, can be expected to develop persistent dimers. By contrast, in aqueous systems each of the carboxyl groups would be able to associate with the much more numerous water molecules. Thus, persistent dimers of the type shown in Part B would not be expected in aqueous systems.

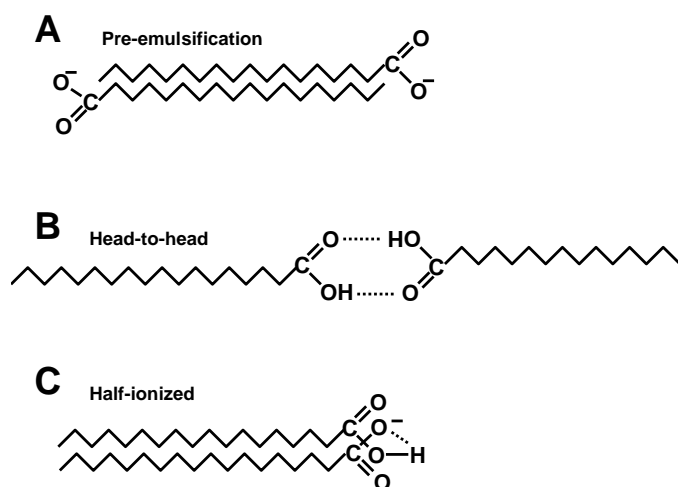


Fig. 6. Three proposed modes of dimerization of compounds related to fatty acids. A: proposed pre-micellization step at concentrations below the CMC; B: proposed association between pairs of protonated carboxylic acids by hydrogen bonding, especially in non-aqueous media; C: proposed association between a charged and an uncharged fatty acid moiety, especially when held in close proximity as a result of mutual association of fatty acid tail groups

Association between Carboxyl and Carboxylate Groups

Note that Part C of Fig. 6 suggests the presence of hydrogen bonding between the proton associated with one of the carboxyl groups and an oxygen belonging to the adjacent carboxylate group. Such an association has been proposed to play an important role in systems where mixtures of protonated and dissociated fatty acids are both present (Nyrén and Back 1958a; Goddard and Ackilli 1963; Goddard *et al.* 1966; Lieckfeldt *et al.* 1994; Back 2000; Kanicky *et al.* 2000; Kanicky and Shah 2002; Vercoe *et al.* 2004; McLean *et al.* 2005b; Dhathathreyan 2008; Strand 2013; Wellen *et al.* 2017).

Evidence in favor of relatively stable structures in which protonated and dissociated carboxyl groups are hydrogen bonded was presented by Binks (1991). However, the effect can be perceived more clearly if the plotted line is drawn differently from how it originally appears in the cited work. Figure 7 has been redrawn here such that the plotted line corresponds more accurately to the data points, compared to the original publication. As shown, there is a relatively horizontal section of the plotted solid line, which suggests a relatively constant composition of the monolayer within the pH range between about 6 and 9. Related findings have been reported by Goddard and Ackilli (1963) and Goddard *et al.* (1966). It has been proposed that a near-constant value of surface potential (ΔV) would

result from a stable composition, which might be proposed to involve a 50:50 mixture of charged and uncharged fatty acid species (Kanicky and Shah 2002). Strand (2013) reported that the packing of fatty acid micelles was most dense near to the pK_a value, where a 50% ionized mixture would be expected. Kanicky *et al.* (2000) reported that near to the pK_a value there was minimum evaporation of water, maximum foam stabilization, a minimum contact angle on a plastic surface, and a maximum surface viscosity. All of these findings are consistent with a stable composition that also favors the integrity and close packing of the spread films.

The concept just described does not fit all published findings. For instance, Sanders and Spink (1955) and Betts and Pethica (1956) described a nearly linear change in the ratio of protonated to dissociated carboxyl groups in fatty acid monolayers at the water surface as the pH was raised in the range 4 to 8.5. In those cases there was no reported preference for a 1:1 ratio of protonated and dissociated carboxyl groups. Further work may be needed to determine whether there are other yet-unknown factors affecting such results.

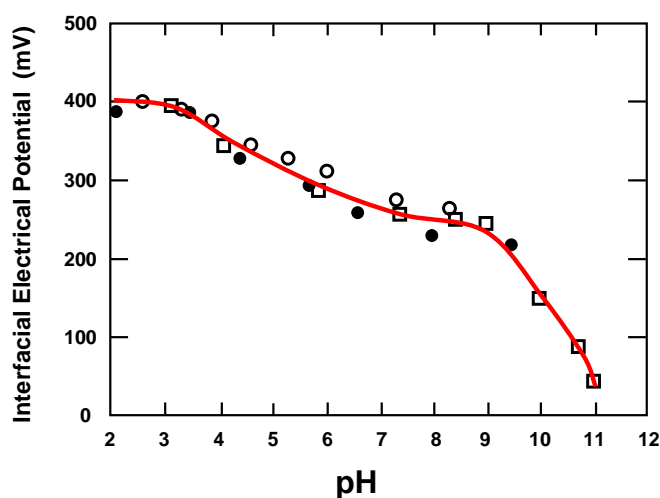


Fig. 7. Interfacial change in electrical potential across a fatty acid monolayer as a function of pH (replotted from Binks 1991)

PITCH PROBLEMS AND CONTROL

Pitch-related Problems in Pulp and Paper Mills

An initial motivation for writing the present review article was to better understand and help efforts to overcome practical problems of pitch deposition in pulp and paper mills. As noted in earlier review articles on the topic, some of the most effective pitch-control measures involve deposition of wood extractives onto surfaces such as fibers or talc; alternatively, the aqueous conditions can be adjusted such that the extractives will tend to remain in stable suspension (Hassler 1988; Laubach and Greer 1991; Back 2000; Hubbe *et al.* 2006; McLean 2008; Tanase-Opedal *et al.* 2011a; Richardson *et al.* 2012; Strand 2013).

From the perspective of a pulp and paper manufacturer, much of the challenge presented by pitch deposition problems is related to the complexity and changing composition of wood extractives entering and passing through the system. Resin acids and terpenes, which often comprise about 0.6 to 0.9% of the dry mass of conifers used for

pulping (Fengel and Wegener 1984), are often the major component in pitch-like deposits on papermaking equipment and related spots on the paper product (Back 2000; McLean *et al.* 2005b; McLean 2008; Strand 2013). As noted by Back (2000) and MacNeil *et al.* (2011), the resin acids are generally more water-soluble but more viscous than the fatty acids. Triglyceride esters of fatty acids are especially prominent in fresh wood chips and in wood harvested in the wintertime in temperate climates (Blazey *et al.* 2002). With generally warmer temperatures in recent years, there has been a trend toward lower ratios of triglyceride esters to free fatty acids, even in winter months (Stack *et al.* 2019b). Thus, with projected continuing warming of the world's climate, one can expect there to be an increasingly prominent role played by the free fatty acids. A high ratio of triglycerides to fatty acids in wood chips often correlates with greater severity of pitch problems in pulp and paper mills (Fisher and Messner 1992; Blazey *et al.* 2002; Richardson *et al.* 2012). On the other hand, extractives that have a low ester-to-acid ratio are susceptible to deposit problems, depending on the pH and the presence of hardness ions in the water (Stack *et al.* 2019b). Recent anecdotal information from paper mills indicates that more problematic pitch deposition episodes are happening during the summer, when a greater proportion of the triglycerides have been hydrolyzed to their corresponding fatty acid form (Stack *et al.* 2019b). Due to their very hydrophobic nature, the triglycerides are typically present in the core of pitch emulsion droplets (Qin *et al.* 2004; Vercoe *et al.* 2004; Lee *et al.* 2011; Richardson *et al.* 2012; Strand 2013). Low-mass unsaponifiable compounds, such as α -pinene, sometimes are not present in typical pitch particles due to their high volatility.

Figure 8, which is presented here for the first time, represents the kind of emulsion droplet that might be present in a pulp and paper facility that processes both hardwood and softwood pulps. The resin acids shown in the figure would come from the softwood, whereas the triglycerides would come from either hardwood or softwood sources.

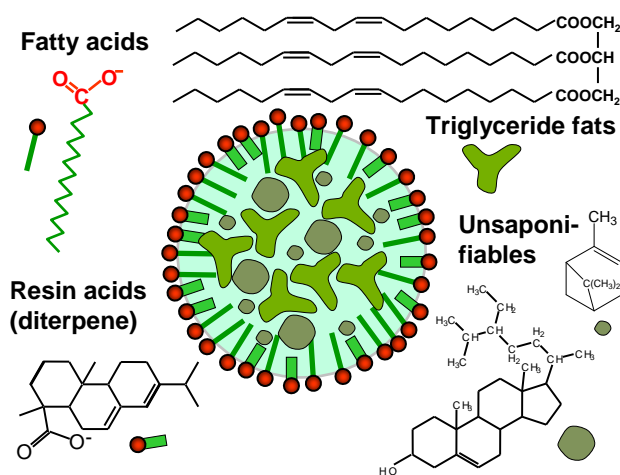


Fig. 8. Expected segregation of components within pitch droplets in a typical papermaking system, such that the more hydrophobic components are in the core and the more polar components tend to be on the outside. The unsaponifiable compounds depicted at the lower right are α -pinene (pine oil) and β -sitosterol.

As illustrated, the fatty acids, along with resin acids, will tend to populate the outsides of pitch droplets, where they would be expected to play a big role with respect to the initial deposition of pitch onto various surfaces. Polysaccharides, *i.e.* hemicellulose-related chains, often act as a stabilizer for the pitch particles in pulp and paper mill systems

(Sihvonen *et al.* 1998; Back 2000; Maher *et al.* 2007; Strand *et al.* 2011a,b). However, divalent metal ions, especially Ca^{2+} and Mg^{2+} , tend to reverse such stabilizing effects (Sundberg *et al.* 1994c; Sihvonen *et al.* 1998; Saarimaa *et al.* 2006; Strand *et al.* 2011a). Regression analysis by Stack *et al.* (2019a) showed that thermomechanical pulp mixtures with a low ester-to-acid-ratio were susceptible to destabilization in the presence of hardness ions when the pH was above 5.5. Some of these effects can be predicted by measuring the zeta potential, which gives an indication of whether or not the droplets will be stabilized by repulsive electrostatic forces (Back 2000).

pH shock

The immediate blame for a new episode of pitch deposition in a pulp and paper mill is often placed on some form of shock, meaning that some measurable parameter changes abruptly at some point in the process. In particular, abrupt changes in pH often take the blame for pitch deposits, especially when they occur at localized points in the process (Gustafsson *et al.* 1952; Allen 1988; Allen *et al.* 1998; Laubach and Greer 1991).

Confirmation of the harmful influence of upward spikes in pH in a mechanical pulp system were obtained in a newsprint paper mill (Allen *et al.* 1997; 1998). High levels of aluminum were found in the pitch deposits. Initially it was thought that the deposits might have been precipitated by the dissolution of aluminum from clay that was being used. However, the problem was eventually narrowed down to the high pH of the clay suspensions. The high pH of the clay slurry apparently brought about sufficient dissociation of the fatty acid monolayers so that the fatty acids were released into solution in the soap form. This is consistent with the findings of Ekman *et al.* (1990), who showed that the concentration of fatty acid moieties in solution was doubled when the pH of a mechanical pulp mixture was increased from 5 to 8. Sundberg *et al.* (1994c) noted that peroxide bleaching is another common cause of upward spikes in pH in mechanical pulp systems, which can lead to pitch deposit problems. The effect was attributed to the deacetylation of glactoglucomannans. Following the deacetylation, the hemicellulosic material became adsorbed onto fibers rather than playing its original role in the stabilization of pitch emulsion particles. Matulis and Bloomfield (2001a) noted that fatty acids and amines are especially susceptible to pH shocks. Fatty amines were found to switch from being almost completely soluble at very low pH to almost insoluble after titration with NaOH to the uncharged state. Stack *et al.* (2015) showed that disturbances to pH with an increase and then decrease back to starting pH resulted in a change in the nature of the extractives. Notably, it was found that an upward excursion of pH by itself, without being followed by a return to lower pH, did not result in pitch deposition.

Water hardness shock

The other type of change in paper mill systems that gets blamed for pitch deposition involves addition of divalent ions. The following articles describe cases in which the presence of Ca^{2+} and/or Mg^{2+} was an essential factor in bringing about pitch deposition in pulp and paper mills (Gustafsson *et al.* 1952; 1954; Swanson and Cordingley 1956; Örså *et al.* 1977; Allen 1988; Sundberg *et al.* 1994b,c; Sihvonen *et al.* 1998; Lindström *et al.* 1988; Lee *et al.* 2011; MacNeil *et al.* 2011; Strand 2011a; Richardson *et al.* 2012). These effects might be attributed to an interaction between the divalent ions and the soap form of fatty acids (Sundberg *et al.* 1994c), as outlined above. Such interactions can be expected to convert the material from a soluble form to a tacky, insoluble form. For instance, Sundberg *et al.* (1994c) showed that an increasing concentration of CaCl_2 in the range 1 to

10 mM caused a mixture of colloiddally stable wood pitch particles to become almost completely precipitated, leading to sedimentation. Though other compounds, such as resin acids present in their soap form, also can be involved, it is proposed here that fatty acids, due to their tendency to become soluble when the pH reaches a critical value, can play a trigger-type role in bringing about such deposition.

Combined effect of pH spike and presence of divalent ions

Based on the concepts discussed in the first part of this article, it is possible to suggest an initial explanation of pitch deposition problems brought about by pH shock, especially when calcium or magnesium ions are present in the aqueous phase. As shown in Fig. 9, which is published here for the first time, the mutual association among the alkyl groups of the fatty acid molecules within monolayers can be expected to keep the fatty acids in a stabilized state – either uncharged or 50% charged – at pH values as much as three units higher (McLean *et al.* 2005a; Strand 2013) than the pK_a values of typical carboxylic acids (Mesmer *et al.* 1989). In other words, one can visualize that there may be a stable colloidal suspension present initially, as represented by the upper left part of Fig. 9. Then, a sufficiently high excursion in pH can be expected to result in a chaotic system, as the monolayer films at the surfaces of emulsified pitch droplets abruptly lose their stability. Freshly released fatty acid soaps immediately become vulnerable to interaction with calcium or aluminum ions, rendering them insoluble once again (Gustafsson *et al.* 1954; Swanson and Cordingley 1956). As shown in the figure, the released fatty acids can be expected to form hard-to-reverse complexes with multivalent ions (Kubicki *et al.* 1999). The composition of material, in its final macroscopic form, may be almost the same as its initial composition; however, the momentary excursion to a higher pH is proposed to serve as an enabling step, giving rise to a more chaotic, tackier, and larger irreversible structure of depositable extractives. The process is essentially irreversible, since the deposited material cannot be easily converted back into a colloiddally dispersed, stable form.

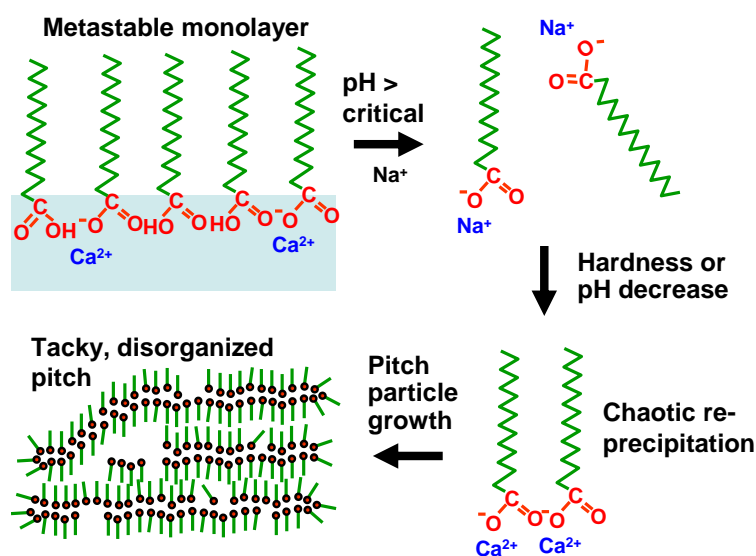


Fig. 9. Proposed mechanism to account for reported episodes of pitch deposition in paper mills initiated by upward excursions of pH when there are divalent ions in solution

Though the mechanism just described is generally consistent with many of the research findings already cited in this article, it does not account for all aspects of pitch deposition. In particular, it has been shown recently that effects related to hemicellulose components may overwhelm the expected influence of calcium, relative to the deposition of pitch from a peroxide-bleached thermomechanical pulp suspension (Stack *et al.* 2019a,b). Also, the overall tendencies of pitch deposition tend to be different depending on whether or not the pitch episodes are dominated by resin acids. Dreisbach and Michalopoulos (1989) noted that fatty acids tend to exhibit maximum deposit problem in paper mills at neutral pH and low temperature, whereas resin acids showed low deposition under those same conditions.

Mechanical effects

Though the chemical-based mechanism just described provides a rationale for why pH shock and the presence or increased level of divalent ions are often associated with pitch deposition in pulp and paper mills, mechanical factors also appear to play a significant role. Swanson and Cordingley (1956) proposed that multilayer films of the type discovered by Langmuir and Blodgett (1935) and Blodgett and Langmuir (1937) can serve as a mechanism of pitch deposition. Langmuir and Blodgett discovered that cyclic raising and lowering of the water level in a system in which there was a condensed monolayer film of stearate molecules at the air-water interface resulted in build-up of multilayer films. It was proposed by Swanson and Cordingley (1956) that in pulp and paper mills a similar effect can take place due to rhythmic lapping wave action, such as might occur at the side of a chest. The mechanism is illustrated in Fig. 10. The material built up due to such “bathtub ring” deposition would then be susceptible to re-entrainment into the papermaking process, leading to deposits onto sensitive parts of the paper machine, such as at the headbox, forming fabric, press felts, transfer rolls, and dryer can surfaces. The cited authors suggested that the relatively brittle nature of fatty acid soap films stabilized by the presence of divalent ions or aluminum ions can favor crumpling of the material, leading to the formation of a tacky, insoluble, macroscopic deposit. Indeed, work by Angelova *et al.* (1994) showed a highly hydrophobic nature of such multilayers.

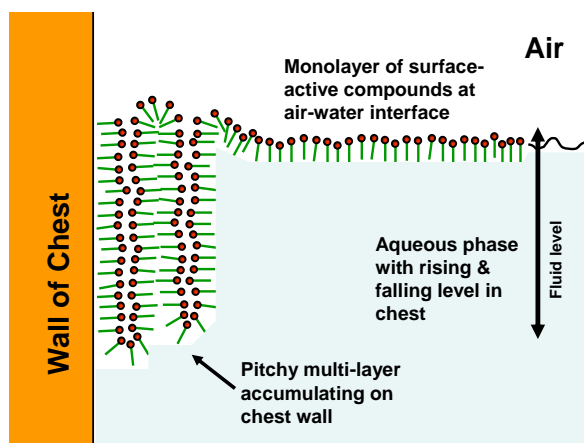


Fig. 10. Mechanism of Langmuir-Blodgett multilayer film deposition resulting from cycled raising and lowering of water level in the presence of a spread fatty acid (or mixed) monolayer film in the presence of stabilizing ions, such as divalent cations

The mechanism shown in Fig. 10 should not be assumed to account for all pitch deposit problems in paper mills resulting from mechanical phenomena. There are other mechanical factors that likewise would be expected to promote the buildup of pitch. For example, the collapse of foam bubbles (see Fig. 11) can provide another mechanism by which monolayers of fatty acid soap molecules, sometimes stabilized by calcium or aluminum ions, can build up as multilayers (Allen 1980). Another mechanism, which is especially applicable to papermaking systems, consists of repeated contact between rotating surfaces, paper, and fabric surfaces. By such a mechanism, wood resins released from parenchyma cells can be transferred from the paper to other surfaces, leading to the filling of press felts or the creation of tacky areas on transfer rolls in the paper machine system (Hubbe *et al.* 2006). Also, the presence of cooler surfaces within a paper mill system might serve as the trigger for extractive materials to form deposits (Richardson *et al.* 2012; Stack *et al.* 2019a,b).

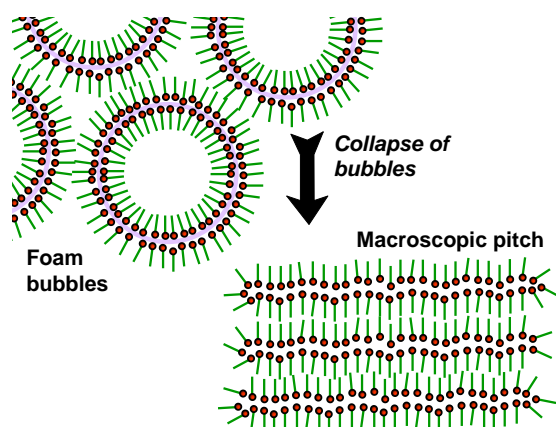


Fig. 11. Conceptual diagram suggesting how the collapse of foam bubbles can be hypothesized as a way that monolayers of fatty acids and other components of wood extractives could be transformed into multi-layer, macroscopic pitch structures

Proactive Pitch Management

Earlier review articles already have described a wide range of strategies that have shown promise in minimizing pitch deposition in a variety of different kinds of papermaking operations (Hassler 1988; Laubach and Greer 1991; Allen 2000b; Back 2000; Hubbe *et al.* 2006; McLean 2008). Here the focus is on looking for possible connections between the effects of such strategies and the reported tendency of the fatty acid component to form dense monolayer films, as well as the consequent shifts in pK_a values and related behavior.

Seasoning

Pitch problems on paper machines have been reported to be less severe if the wood chips used for pulping have had more time to season (Laubach and Greer 1991; Gutiérrez *et al.* 1998). The usual explanation for these effects is that seasoning allows the progress of enzymatic action, which promotes oxidation of sterols and hydrolysis of triglycerides (Gustafsson *et al.* 1954; Laubach and Greer 1991; Gutiérrez *et al.* 1998). The latter reaction is notable in this context of this article, since it suggests that the more oleophilic ester form of fatty acids – the triglyceride fats – is typically a greater cause of pitch problems than the fatty acid soaps or protonated species that result from the hydrolysis reactions. On the

other hand, papermaking experience has shown that abrupt substantial conversion of triglycerides to fatty acids, brought about by treatment with lipase enzymes, also can lead to severe pitch deposit problems in paper mill systems. This is an area where additional research would be helpful.

Strand *et al.* (2011b) reported related results dealing with the pH at which one-half of the fatty acids and resin acids were in the dissolved phase, *i.e.* the pK_{lw} values. It was observed that the pK_{lw} values of fatty and resin acids were noticeably lower in pitch emulsions with a low content of triglycerides (ratio of triglycerides(TG) : resin acids(RA) : fatty acids(FA) = 2.0:1.5:1.0), compared to in pitch emulsions containing a high amount of triglycerides (TG:RA:FA: 5.1:1.5:1.0). This observation was accredited to formation of possible FA-RA aggregates in the water phase that were able to pass through a 0.1 μ m filter. It was suggested that if there is a lack of suitable surfaces for the fatty and resin acids to rest upon, they will be pushed out into the water phase, even below their pK_a . In the water phase, they should have the opportunity to be much more susceptible to pitch-forming interactions than the FA/RA attached to a colloidal entity. Similar findings were later reported by Lee (2011) and Richardson *et al.* (2012). These authors claimed that a low ratio of triglycerides to resin and fatty acids actually altered the structure of pitch droplets, creating separate layers of resin acids and fatty acids.

Deresination

Another pro-active approach that pulp and paper manufacturers can take in an effort to overcome pitch deposition problems is to actively separate wood resins from the pulp. This can be achieved, for instance, by increasing the pH of high-yield pulp ahead of a washing operation (Ekman *et al.* 1990; Suckling *et al.* 1990). Suckling *et al.* (1990) reported the greatest increases in wood resin solubility associated with pH increases within the range 6 to 9, which is consistent with the pK_a values associated with fatty acids under various conditions of salt and/or multivalent ions. Presumably, the adjustment of pH to well above the pK_a values of carboxylic acid components of the wood resins promotes their release as a micellar solution that can be washed from the fibers. The high pH associated with kraft pulping is likewise known to be favorable for bringing about the release of pitch-like materials from pulp fibers (Lindström *et al.* 1988). Kraft pulping conditions also bring about hydrolysis (converting triglyceride fats to fatty acid soaps, glycerin, and sterols), as well as other reactions leading to degradation and polymerization. The cited study noted that the released extractives may tend to precipitate again onto the pulp fibers in the final stage of brown-stock washing as a result of there being a less alkaline pH at that stage. Ström *et al.* (1990) observed the highest solubility (which can be regarded as washability) in mixtures of fatty acids and resin acids, at moderate ionic strength.

There are a few practical ways to deal with pitch-contaminated process water obtained from the washing of pulp. In an integrated pulp and paper mill, a goal is to send most of the organic solids washed from the pulp to a chemical recovery system. Another option, especially if the water contains chlorides or other species incompatible with a chemical recovery plant, is to send the filtrate from pulp washing to wastewater treatment. Alternatively, the surface-active compounds and hydrophobic matter can be separated by dissolved air or induced air flotation (Negro *et al.* 2005; Korpela 2006; Tanase-Opedal *et al.* 2011a,b; Strand *et al.* 2012; Zasadowski *et al.* 2013; Singh *et al.* 2016). Zasadowski *et al.* (2013) showed that induced air flotation, carried out under optimized conditions of pH and other variables, could remove 90% of the pitch-forming matter and up to 70% of pectic acids, which contribute to a high cationic demand of the furnish. Reduced pH conditions

were found to be favorable for such separations (Strand *et al.* 2012; Zasadowski *et al.* 2013). At the same time, the induced air flotation did not tend to remove most of the hemicellulose content, which is known to contribute to inter-fiber bonding in paper. The flotation-based strategies take advantage of the surface-active nature of the fatty acids and some other compounds that papermakers would want removed from their process water. Because bubbles tend to be stabilized by monolayer films of surface-active molecules, including fatty and resin acids, the earlier discussions of the role of fatty acid and their soaps in such monolayers are highly relevant. Based on the earlier discussions, one can expect that the successful operation of dissolved air flotation may require stable aqueous conditions. This would include stable values of pH, salt concentrations, and levels of multivalent cations.

Additives for Control of Pitch during Papermaking

The behavior of the fatty acid component of the wood extractives also can be considered in the light of pitch-control strategies that have been found to be effective during papermaking (Hassler 1988; Laubach and Greer 1991; Hubbe *et al.* 2006). One of the frequent recommendations to minimize pitch deposits in mechanical pulp systems has been to avoid excursions of pH above a critical value (Gustafsson *et al.* 1952, 1954; Allen 1988; Allen *et al.* 1998; Laubach and Greer 1991). Such advice is consistent with the mechanism described earlier, associated with Fig. 9. As described earlier, the mutual association within monolayers rich in fatty acids are often present in a meta-stable state, such that a spike of higher pH, followed by a return to lower pH in the presence of divalent or higher-valent cations can be expected to cause an irreversible change to a much tackier and problematic pitch situation in the paper mill.

Some of the most reliable measures carried out in paper mills to address pitch deposition problems involve the use of mineral particles, such as talc (Hubbe *et al.* 2006; Gantenbein *et al.* 2010). Two tendencies appear to be responsible for the affinity of wood resin particles for various mineral surfaces. First, relatively hydrophobic minerals such as talc can be expected to preferentially collect hydrophobic materials. This is consistent with the discussion of the hydrophobic effect in the theory section of this article. Second, when mineral surfaces either have a positive charge or have been treated to make them positive (Lamar *et al.* 1990; Hyder *et al.* 1991; Bouffard and Duff 1999; Tanase-Opedal 2011a), they can collect pitch particles that are negative in charge mainly due to the presence of carboxylic acid groups.

Though the references cited in the previous paragraph generally envision a process of pitch droplets or agglomerates adsorbing onto and remaining stuck to the mineral surfaces, it makes logical sense also to expect the formation of monolayers of fatty acid soaps onto such surfaces. Self-assembly of such layers would be favored by the same circumstances that lead to such layers at air-water interfaces and at the surfaces of micelles and emulsion droplets: Though the talc surface is not as hydrophobic as air itself, it represents a surface to which there is relatively little contribution of hydrogen bonding. It follows that thermodynamics will favor structures in which the hydrophobic mineral surface is facing the non-polar part of a monolayer film. In support of the concept that the hydrophobic character of the mineral can be important, it has been shown that the beneficial effect of talc can be defeated in some systems if talc becomes covered by hydrophilic polymers (Gantenbein *et al.* 2010).

The adsorption of extractives onto mineral surfaces is consistent with the results of flow cytometry experiments (Richardson and Grubb 2013). In the cited work, interactions

were investigated between colloidal wood pitch and various inorganic particles (precipitated calcium carbonate, ground calcium carbonate, kaolin, and bentonite). By measuring the hydrophobicity of filler particles (hydrophilic) mixed with colloidal wood pitch (hydrophobic), it was possible to see that the mixture formed a population of intermediate hydrophobicity; *i.e.* the hydrophobic wood pitch happily interacted with hydrophilic filler particles in suspension. Furthermore, it was shown that these interactions could be inhibited to a certain extent by the introduction of steric stabilization to the system (the presence of water-soluble galactoglucomannans). The steric stabilization decreased the risk of collisions between pitch and filler particles and actually decreased the hydrophobicity of the resulting intermediate population.

Aluminum sulfate

Effects related to aluminum, in various forms, are of great interest in light of the widespread use of aluminum sulfate (papermaker's alum) and related additives in papermaking processes. In particular, aluminum sulfate is used sequentially with the addition of rosin size products in their emulsified acid and soap forms to render the paper hydrophobic (Strazdins 1977, 1989a; Marton 1989; Kitaoka *et al.* 1995, 1997). Alum is also used by papermakers to promote dewatering, to promote fine-particle retention, and to precipitate wood resins and other colloidal matter onto fiber surfaces (Strazdins 1989a). Hassler (1988) noted that alum generally has favorable effects, mitigating pitch problems, in systems where the pH is near to 5, favoring the presence of positively charged ionic forms.

It has been found that alum can be effective for precipitating resinous compounds such as the hydrolysate of alkenylsuccinic anhydride (ASA) sizing agent onto the surfaces of fibers, allowing such materials to be purged from the paper machine system. Scalfarotto (1985) showed that such precipitates tended to be less tacky in comparison to the corresponding precipitates resulting from interaction with calcium or especially with magnesium divalent cations. The difference is consistent with the higher valency of the alum and its related oligomers (Bottero and Fiessinger 1989; Bi *et al.* 2004). As a result of the higher valency, the insolubilized matter takes on a net positive charge and is attracted to the predominantly negatively charged surfaces of the fibers. Solid-like monolayer films are formed in the presence of aluminum ions, compared to divalent metal ions (Swanson and Cordingley 1956). Such a difference suggests that the precipitated material will be less tacky and less likely to cause deposition issues.

High-charge cationic polymers

Based on the strong complexing interactions observed between the soap forms of wood resins and alum, as just described, one would anticipate strong interactions also in the case of high-charge-density cationic polyelectrolytes. Indeed, such polymers have been found to be effective in some cases in addressing pitch problems in paper mill systems (Sundberg *et al.* 1994a; Hubbe *et al.* 2006; Maher *et al.* 2007; McLean 2008; McLean *et al.* 2010). However, the success of different cationic polymers in stabilizing the pitch particles and in retaining them onto fiber surfaces have been found to be very different, and there does not seem to be an easy way to predict which polymer would be effective (Maher *et al.* 2007; McLean 2008; McLean *et al.* 2010). Such diversity of effects is consistent with the role of fatty acids in suppressing transitions from one physical state (such as a fully or half-protonated monolayer film) to another state (such as chaotic breakdown of a monolayer film above a critical pH value). In cases where the fatty acids

are essentially holding back a potential chaotic transition, leading to deposition of tacky material, one can expect it to be difficult to predict reliable treatments to overcome pitch deposition problems by use of different cationic polymers.

Enzymatic treatments

Over the past several years, enzymatic treatments have become increasingly used in pulp and paper systems for a variety of purposes (Hubbe *et al.* 2018). One such approach involves treatment of pulp slurries with lipase, an enzyme that cleaves the ester bonds in triglyceride fats, converting them into a mixture of glycerol and free fatty acids (Fisher and Messner 1992; Fujita *et al.* 1992). Fisher and Messner (1992) described a process in which, after the enzymatic hydrolysis of the triglycerides, the released fatty acids were extracted by treatment with NaOH and washing of the pulp. Fujita *et al.* (1992) described a simpler system in which the released fatty acids were simply left in the papermaking process; notably the net effect was a reduction in pitch problems in the case studied. Due to the potential for a variety of interactions among different wood resin moieties, metal ions, pH conditions, and interactions with different solids surfaces, this is a topic that merits more extensive research.

A lesser-known type of enzyme called lipoxygenase plays a key role in the shortening of the hydrophobic tails of multiply-unsaturated fatty acids and their esters, *e.g.* compounds that comprise linoleic and linolenic groups (Zhang *et al.* 2005, 2007). Work by Tayeb *et al.* (2017c) showed that treatment of such unsaturated fatty acids with lipoxygenase was able to shorten them. The mechanism is illustrated in Fig. 12. In related work it was shown that such treatment decreased the deposition of unsaturated fatty acids under laboratory (Tayeb *et al.* 2017b) and pilot plant (Tayeb *et al.* 2017a) conditions. Such results are consistent with a mechanism whereby the tendency of self-association of the alkyl tails – which would be weakened by this type of enzymatic treatment –contributes to the deposition tendency of the material under suitable conditions. The mechanism indicated in Fig. 12 also can be expected to occur during storage of wood chips.

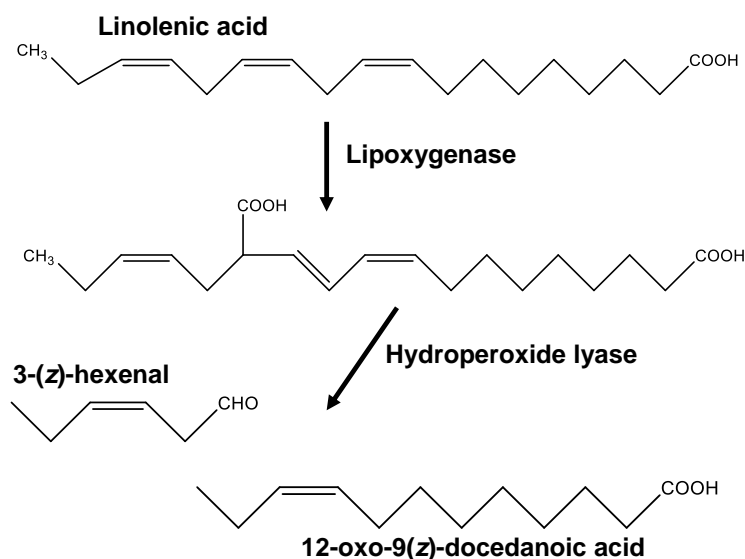


Fig. 12. Mechanism of enzymatic shortening of the tails of unsaturated fatty acids

SIZING STRATEGIES INVOLVING FATTY ACIDS

Motivation: Inexpensive and Environmentally Friendly

There are strong motivations to consider fatty acids and their soaps as potential sizing agents for papermaking. They are widely available and low in cost. Their potential sources include not only vegetable oils, but also the alkaline pulping of wood (Jansson and Wadsborn 2007). As a compound widely present in the environment, fatty acids and their soaps are not regarded as significant environmental risks.

There are two essential characteristics of any chemical compound that is intended to act efficiently in rendering paper resistant to the spreading and permeation by aqueous fluids (Davison 1976; Dumas 1981). First, the compound needs to include a hydrophobic part. Second, it needs to have a means of becoming anchored to fibers. In the case of rosin soap sizing systems, the anchoring system is provided by carboxylate groups, which interact with aluminum ions and then help bind the precipitated material to fiber surfaces (Strazdins 1977; Marton 1989). The situation just described begs the question: Since fatty acids have a hydrophobic group, connected to a fatty acid, why have they not become more prominent as a means of imparting water resistance to paper products? Rather, as noted by Strazdins (1989b), the presence of fatty acids in the formulation hurts the effectiveness of rosin sizing. The deleterious effect of fatty acids on rosin sizing is observed especially in the case of unsaturated species, such as oleic, linoleic, and linolenic acids.

A search of the patent literature revealed only one disclosure of a paper hydrophobic sizing system based on fatty acids. Martin (1981), representing the Eastman Kodak company, claimed a system whereby the soap form of a long-chain fatty acid is precipitated by a metal ion, preferably chromium. The alkyl chain is claimed to have a length within 12 to 22, which is consistent with development of an association tendency within a monolayer. The inventor showed that treatment of paper with such a system could inhibit subsequent staining of the paper by the next dye to which it was exposed. No related patents were found, so it is unclear whether or not the system achieved its desired ends in an effective manner.

Shimada *et al.* (1997) compared results for several different fatty acids, using either alum or a high-charged cationic polymer (polyallylamine) to set the size. Isocyanates were also compared, as a means to create covalent attachments so that the effects of different tails could be compared for firmly bound hydrophobic chains. The authors observed instances of poor sizing performance with C18 moieties, which they attributed to poor distribution of the compound within the paper sheet. They attributed the much better performance of rosin (in combination with alum treatment) to a bulky molecular structure that serves to protect the ionic linkage created by the aluminum, especially when the wetting solution was acidic due to the presence of lactic acid. In the case of fatty acids, effective sizing was generally observed at a pH of 4 in the presence of alum, with the requirement that the fatty acid moiety needed to have at least 10 carbon atoms in the tail. One of the unique findings was that, unlike popular sizing systems involving addition of the agent to the fiber slurry (Hubbe 2014), the treatment resulted in markedly reduced paper strength. Such an effect is consistent with the bound fatty acid layer getting in the way of potential hydrogen bond formation between the fibers in the course of drying of the paper. It is logical to expect that preparation of a waxy layer of stearic acid-type chains, especially if present as a condensed monolayer, would be detrimental to later efforts at bonding or for adhesion of the resulting paper to other surfaces. Poor adhesion and slipperiness problems have been observed in the case of sizing with alkylketene dimer, another system for

hydrophobic sizing that involves saturated chains of stearic acid (Brungardt and Gast 1996; Hubbe 2007). Likewise, poor adhesion of xerographic toner was been reported when using a type of polyurethane with long-chain alkyl substituents during the surface-sizing of paper (Batton 1992; Hubbe 2007).

More recent efforts have been reported, obtained in the research laboratory to develop and demonstrate a sizing system based on fatty acids as a key component (Kitaoka *et al.* 2001; Ohno *et al.* 2002). The approach employed by Ohno *et al.* (2002) more closely resembled the practices of rosin soap sizing (Marton 1989). Thus, handsheets were prepared by treating a pulp suspension with fatty acid soaps, followed by alum. When deionized water was used to prepare the suspension, the main form of fatty acids present in the resulting paper was free fatty acids, despite the fact that the sheets were prepared in the presence of aluminum ions. When water of ordinary hardness was used in preparing the sheets, the calcium salts of the fatty acids were the main form of fatty acids in the paper, leading to hydrophobic sizing. There was also a linear correlation between the retention of fatty acids in the paper and the amount of calcium ending up in the sheets. These results suggest that a poor ability of fatty acid soaps to interact with aluminum ions in aqueous solution may be one reason why such systems have not been more successful.

Kitaoka *et al.* (2001) prepared base paper with aluminum sulfate, and then they dipped the sheets into a fatty acid emulsion stabilized by nonionic surfactant. The emulsion droplets had a negative charge, which was attributed to at least partial dissociation of the fatty acid to the soap form. Hydrophobic paper was obtained, especially in cases where the dipped paper was air-dried, then cured in an oven. It was also found that a highly charged cationic polymer, polyamidoamine-epichlorohydrin, could be used in place of the alum to achieve a sizing effect. These results are consistent with the self-assembly of fatty acid soap as a monolayer during drying and curing. Figure 13 provides a schematic concept for such a process. The fact that pretreatment of the pulp with alum or high-charge cationic polymer was needed for effective hydrophobic sizing is consistent with the stabilizing effect of aluminum ions on spread monolayer films (Swanson and Cordingley 1956).

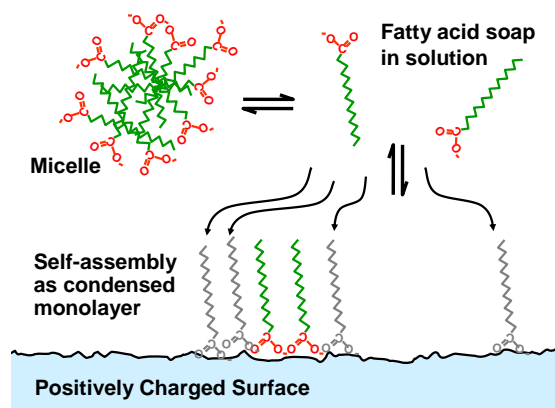


Fig. 13. Concept of self-assembly of charged surfactant molecules into a condensed layer onto an oppositely charged substrate

Success in creating hydrophobic surfaces also has been achieved for some other systems in which the surface to be hydrophobized was first provided with a strong positive ionic charge (Touwslager and Sondag 1994; Liascukiene *et al.* 2014). The cited authors used oxidized aluminum as a substrate. Such surfaces are known to have positive zeta

potential at low to near-neutral pH values (Pedimonte *et al.* 2014; Liang *et al.* 2017). In such systems it has been shown that the amphiphilic compounds with negatively charged groups are able to self-assemble into a layer that presents a highly hydrophobic character (Liascukiene *et al.* 2014).

Lee and Chen (2003) showed that very hydrophobic surfaces could be created by deposition of Langmuir-Blodgett multilayers of highly ordered monolayer films. Films comprised of stearic acid gave good results, but even higher contact angles of water droplets were reached when using such compounds as octadecylamine, dipalmitoyl phosphatidyl choline, and dimyristoyl phosphatidyl choline. Notably, the aqueous sublayer did not contain added ions, which would have been expected to be helpful in stabilizing the monolayers and helping in the preparation of Langmuir-Blodgett multilayers. The authors noted that the systems with highly ordered monolayers tended to provide the greatest resistance to wetting by water.

Challenge: How to Anchor the Soap Compounds

Notably, in the previous subsection, none of the cited studies demonstrated clear success in being able to hydrophobically treat surfaces by combining fatty acid soaps and aluminum ions, which would be the time-testing procedure by which papermakers have used rosin soap products in the so-called acidic sizing of paper (Strazdins 1977, 1989a; Marton 1989). The findings of Ohno *et al.* (2002) suggest that it is mainly the calcium ions, rather than any aluminum ions present, which form a stable association with spread monolayers of fatty acids in their soap form. Such results suggest a mismatch in the size of the hydrated aluminum ions relative to the position of the carboxylate groups, as dictated by their spacing within a condensed monolayer.

Optimization of pH range for sizing using aluminum compounds

Another kind of mismatch that helps to explain the relative lack of success that has been reported for fatty acid soap-alum sizing systems involves the species of aluminum that could be present and their dependency on pH. As has been shown in various studies, the most effective aluminum ionic species for rosin sizing are either the $\text{Al}(\text{H}_2\text{O})_6^{3+}$ ion that is predominant below a pH of 4 or oligomeric species such as $\text{Al}^{\text{VI}}_{12}(\text{HO})_{24}\text{Al}^{\text{IV}}\text{O}_4(\text{H}_2\text{O})_{12}^{7+}$ (Bottero and Fiessinger 1989) that are typically maximized at a pH between 4.2 and 4.6, depending on the concentration and other factors. However, as discussed earlier, within condensed monolayers of fatty acids, the pK_a values, indicating transitions between the protonated and dissociated forms of carboxyl groups, can be shifted to substantially higher values of pH. The narrowness of the ranges of pH where aluminum oligomeric species are optimized (Bottero and Fiessinger 1989; Strazdins 1989a; Bi *et al.* 2004) in combination with the shifting of the pK_a values of the fatty acids to other values outside of that range as a result of the self-association of the alkyl and alkenyl tails groups, thus provides a further explanation why fatty acids have not emerged as a major sizing agent for the paper industry.

Sizing using cationic agents other than alum

One strategy that might be used to get around to the apparent mismatch between the suitable pH range for sizing with alum and the shifted and sometimes hard to predict pK_a behavior of fatty acids consists of selecting a different metal having different pH behavior of its ionic forms. For instance, since fatty acid soaps form films readily on a copper surface (Ein-Eli 2008), one might run tests with copper ions. Likewise, since fatty acids tend to form very stable monolayer films in association with cadmium ions in an

adjacent water phase (Chen *et al.* 2001), one might consider using cadmium ions, except that there would be concerns regarding its toxicity. Another option might be the chromium ion, which already has been claimed as a suitable hydrophobic sizing system for use in silver emulsion-type photographic technology (Martin 1981). The literature in these areas is very limited, and there remain to be a great many other metal systems that could be evaluated in an attempt to find a practical, reliable, and environmentally friendly hydrophobic sizing system based on fatty acid soaps and a metal-based mordant.

Instability of Fatty Acid Monolayers to Molecular Overturn

Another likely problem, which makes fatty acid layers inherently different from the highly successful rosin-alum sizing system, is the possibility that films of fatty acids might be subject to easy disruption, overturn, or dissolution. Figure 14 provides a schematic definition of what is meant here by the term “overturn”. Evidence of molecular overturn was obtained by Angelova *et al.* (1994), who prepared Langmuir-Blodgett multilayers from long-chain fatty esters. Surprisingly, contact angle experiments yielded essentially the same results irrespective of whether the outermost molecular layer was inward-facing or out-ward facing. The cited authors concluded that regardless of how the multilayers had been prepared, the molecules re-equilibrated themselves when exposed to a droplet of water. Graber *et al.* (2009) reported similar effects of time on the degree of hydrophobicity of soil that had become present due to an interaction of fatty acids and calcium, which served as a bridge to anionic sites on solid particles in the soil. Chen *et al.* (2001) concluded that fatty acid films were relatively unstable to molecular overturn based on observations of large differences in advancing and receding contact angles versus a water phase exposed to a Langmuir-Blodgett multilayer film. However, the cited authors did not consider the use of different multivalent ions, the selection of which hypothetically might be optimized to better stabilize either monolayer or multilayer films.

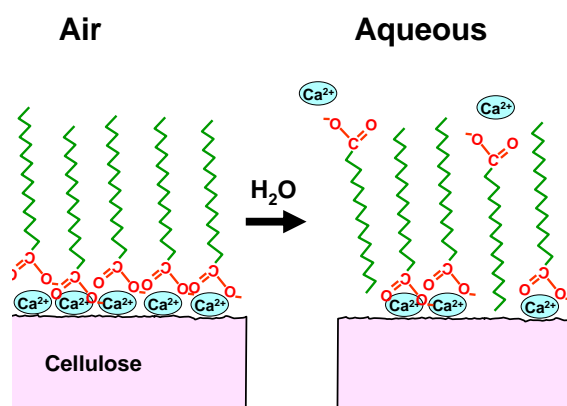


Fig. 14. Concept of “molecular overturn” when a weakly anchored surface-active monolayer is wetted by water

Györvary *et al.* (1996) observed that multilayer films of fatty acid stabilized by cadmium (II) and terbium (III) ions lost their water-repellent character when the pH was raised within the range from 5.4 to 6.7. These observations are consistent with a tendency of fatty acid molecules to become more soluble upon their dissociation to the soap form when the pH is raised above the pK_a value (Christodoulou and Rosano 1968; Örså *et al.* 1997; Sundberg *et al.* 2009). Treatment with relatively high levels of NaOH would tend

to ion-exchange the Na^+ ion in place of multivalent metal ions that would be needed to achieve stabilized monolayer films.

Implications for Reactive Sizing Agents

Reactive sizing agents, such as alkenylsuccinic anhydride (ASA) and alkylketene dimer (AKD) have a completely different (covalent) mode of attachment to cellulosic fiber surfaces, and they differ from fatty acids in not having any carboxylic acid groups. But on the other hand, these reactive sizing agents resemble fatty acids with respect to the hydrophobic tails groups, and it appears that some of the same issues discussed in the first main section of this article also are relevant for the reactive sizing agents and their performance.

One of the interesting contrasts between ASA and AKD is that the commercially successful ASA products have carbon chains often in the range 20 to 24 (Gess and Rende 2005; Hubbe 2007), whereas AKD is typically prepared with stearic acid chains, *i.e.* C18. The differences are highlighted in Fig. 15. There may be a variety of contributing factors to explain such differences; however, it should be noted that ASA typically includes a double bond within the chain (Dumas 1981; Hubbe 2007). As noted earlier, the presence of a double bond (especially in the *cis* conformation) tends to make the chain perform as if it were about two carbons shorter due to the kinking effect (Brito *et al.* 2011). Accordingly, it is reasonable to expect that the optimum length of such a chain in ASA would be somewhat longer than that present in AKD.

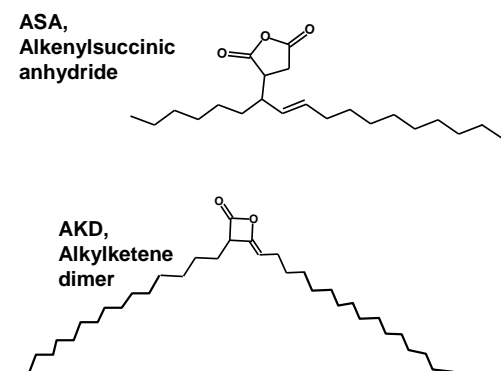


Fig. 15. Molecular structures of alkenylsuccinic anhydride (ASA) and alkylketene dimer (AKD) sizing agents

Another aspect of the two major reactive sizing systems that deserves re-examination in the light of issues considered in this article is whether the effectiveness of ASA and AKD as sizing agents depends on a mechanism in which the alkyl tails remain self-associated, as condensed monolayers, even in the finished paper. Previously it had been sometimes thought that maybe the alkyl tails somehow maximized their influence by being able to “sweep” a wider area on the fiber surface, while still remaining tethered by a covalent attachment to the fiber. But given all of the evidence presented in this article regarding a strong effect of mutual association of such groups, such a sweep model is hard to accept. Another advantage of attributing the effectiveness of AKD at least in part to mutual association of alkyl groups is that it helps to explain why AKD is such an effective sizing agent despite its well-known low reactivity (Dumas 1981; Roberts and Garner 1985; Lindström and Söderberg 1986; Ödberg *et al.* 1987; Brungardt 1997; Isogai 1999). For

instance, it has been shown that paper that has been sized with AKD often contains relatively large portions of unreacted AKD (Roberts and Garner 1985; Bottorf and Sullivan 1993; Bottorf 1994). The fact that nevertheless such paper can be highly hydrophobic is consistent with an understanding that even a minority of covalent attachments to the fibers may be sufficient due to the fact that the mutual association between adjacent alkyl chains will end to hold the hydrophobic layer together and well oriented (Lindström and Söderberg 1986). The concept is illustrated in Fig. 16. The figure is drawn such that there are three ASA molecules that had reacted to form ester bonds with the cellulose surface (or starch adsorbed onto such a surface). But the second ASA molecule from the left in the figure is shown as the calcium salt of the hydrolyzed form of ASA. It is hypothesized that self-association within a condensed monolayer with sufficiently long alkyl chains will tend to hold such a structure together at a fiber surface in sized paper even if some of the molecules are not covalently bound to the surface.

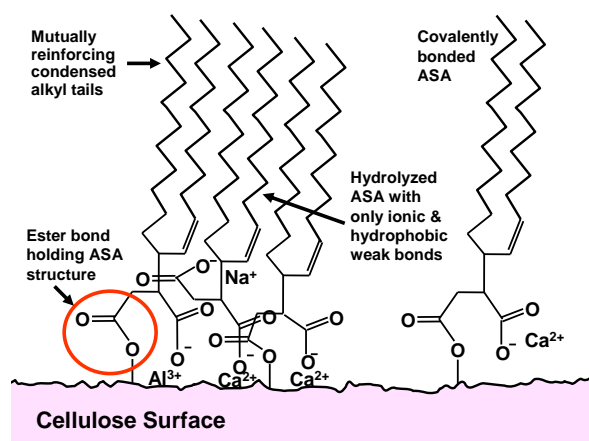


Fig. 16. Concept of hydrophobic sizing, involving ASA sizing agent, wherein the hydrophobic effect can be attributed, at least in part, to condensed, oriented monolayers in which the alkyl chains are facing outwards from the paper surface

It has been noted that when AKD is prepared with unsaturated fatty acid moieties, the resulting size paper is less slippery, which can be an issue at higher levels of treatment with ordinary AKD (Brungardt and Zhang 1999; Karademir *et al.* 2004). However, the effectiveness of the alkenylketene dimer (AeKD) thus formed has been found to be lower than that of regular AKD in bringing about hydrophobization, thus requiring a higher dosage to be used (Brungardt and Zhang 1999). These results provide further support for the concept introduced earlier that double bonds in the hydrophobic chain shorten its effective length (Brito *et al.* 2011). In addition, by making the monolayer film less solid-like, the material is less waxy and does not reduce the coefficient of friction of paper to the extent that AKD can when used at relatively high levels.

The need for further research is highlighted by some contradictory results provided by Smith (1999), who studied the effect of different positions of the double bond in ASA. Surprisingly, the cited author found that the best sizing was achieved when the double bond was centrally located in the ASA, where it would be expected to create a bend in the chain. Less efficient sizing was observed when the double bond was at the end of the alkene used in the ASA synthesis, which would be expected to yield a single straight chain alkyl tail.

BROADER IMPLICATIONS OF ALKYL TAIL ASSOCIATION EFFECTS

While the applications areas that are the main focus of this review article are mainly in the field of papermaking, a couple of examples outside of that field will be covered in this section. There are two reasons to consider such information here. First, some of the reported findings may shed further light on the topics already considered with respect to pitch issues and sizing during papermaking. Second, there may be opportunities to apply what has been learned from papermaking systems to achieve benefits in broader applications.

Soil Wettability

In the field of soil science, Graber *et al.* (2009) showed that interactions involving fatty acid moieties make a significant contribution to rendering certain soil specimens hydrophobic. Consistent with other findings already considered in this article, calcium ions were found to play a role in anchoring fatty acid soap molecules at the soil particle surfaces. Parallel tests in which sodium salts of the fatty acids were used failed to develop hydrophobicity. The authors concluded that the calcium ions acted as bridges between the fatty acid moieties and negatively charged groups on the soil particles, including mineral particles. The rates of overturn of the fatty acids, upon addition to water, was relatively slow. Results also depended on the type of minerals constituting the soil particles.

Hydrophobic Chitosan Sponges

Yodkhum and Phaechamud (2014) prepared hydrophobic chitosan sponges by treating them with aluminum monostearate in a 2% lactic acid solution, followed by heating at 110 °C for 24 hours under vacuum, which was described as dehydrothermal treatment. Such treatment inhibited the swelling of the sponges when they were placed into water. Notably, the effect achieved anchoring that involved aluminum ions. This represents a type of result that Ohno *et al.* (2002) had been unable to achieve when attempting to hydrophobize cellulosic fibers using a conventional soap-sizing strategy, as used by papermakers.

Flotation De-inking

Theander and Pugh (2004) reviewed the mechanism of flotation deinking, a process that is often carried out by adding a combination of fatty acids and calcium chloride to a pulp fiber suspension. It was shown that the process involved encapsulation of the ink particles by precipitation of calcium salts of the fatty acids. The fact that the ink particles were then highly hydrophobic presumably was the explanation for a more effective association with small air bubbles, allowing the ink to be floated up to a froth layer, which was then skimmed from the water surface. This is another example in which the results can be explained by self-association among adjacent alkyl chains, tending to produce a condensed monolayer and leading to a low surface energy.

Protection of Metal against Corrosion

Ein-Eli (2008) studied the use of alkylcarboxylate salts as corrosion-inhibiting agents for copper. Effectiveness was found to increase with increasing alkyl chain length in the range from 3 to 12 carbons. The protective films were found to contain copper carboxylate compounds. The films prevented aggressive ions from being able to access the underlying copper. These results are consistent with two aspects that appear to be

important for the behavior of fatty acids in papermaking system. The findings confirm both the potential anchoring role of divalent metal species and the tendency of long alkyl chains to form dense, contiguous monolayers capable of serving as a hydrophobic barrier.

Superhydrophobic Systems with Fatty Acids

The topic of superhydrophobicity, with application to papermaking systems, was reviewed by Song and Rojas (2013). The term superhydrophobic implies that water droplets on such a surface will have a contact angle of at least 150 degrees and a sliding angle less than 10 degrees. Essential steps in creating a superhydrophobic system are (a) a high degree of roughness, including nano-scale roughness, and (b) hydrophobic treatment of the surface (Hubbe *et al.* 2015). The latter treatment generally has to be sufficient such that a very smooth surface, after subjected to the treatment, would have a contact angle of water greater than 90 degrees. Badre *et al.* (2007) showed that such results could be achieved in a system comprising zinc chloride solution and stearic acid. The deposition system, involving electrochemical deposition, gave rise to nano-rods at the treated surface. Sobhana *et al.* (2017) achieved superhydrophobicity on cellulose fibers by a combination of stearic acid and a double hydroxide. The latter was prepared from equimolar mixtures of silver and aluminum nitrates at various concentrations, where the pH was controlled to 10. The superhydrophobic effect required that the mixing of ingredients take place *in situ*, meaning that the fibers were present during the combining step. Addition of the premixed stearate after reacting with the silver and aluminum ions failed to produce hydrophobic surfaces. Again these results are consistent with the fussy nature of pitch deposition, as described earlier, being dependent on the sequences of events and often involving non-equilibrium transition states and outcomes.

Test Method Development for pK_a Values

There are various potential or existing test methods that can be implemented based on the self-association of long-chain fatty acid moieties. Fu *et al.* (1998) stated that electrophoretic mobility could be used as a way to get information about the pK_a values of fatty acids. The cited authors determined the pK_a values of fatty acid analogues having chain lengths within the range C1 to C10, and all of them (except for some chlorinated compounds) had pK_a values between 4.7 and 5.0. In other words, they did not find any evidence of a colloidal pK_a effect. These results are in disagreement with the findings of Lieckfeldt *et al.* (1995) and Kanicky *et al.* (2000), both of which indicated a strong shift of the pK_a value to substantially higher values with alkyl chain lengths of 8 or more. It is notable, however, that the quantity that Fu *et al.* (1998) were measuring was zeta potential, not pK_a itself. It appears that either the assumptions or the theory developed in the cited work merit re-examination.

CONCLUDING REMARKS

As stated at the outset of this review article, a goal was to focus on the role of self-association among the alkyl or alkenyl tails of fatty acids. Such associations can provide a window by which to try to gain additional understanding of phenomena taking place in papermaking systems. Such phenomena can include pitch deposition in paper mills, challenges related to the potential usage of fatty acids in hydrophobic treatments of surfaces, and some other related applications. The nature of papermaking systems is

complicated, involving multiple surface-active compounds present simultaneously, as well as poorly characterized mixtures of metal ions, varying pH levels, various temperatures, and a range of different contact times and orders of addition. It follows that it would be unrealistic to expect that focus on the fatty acids – which are often a relatively minor component of wood resins present in such systems – would provide easy explanations of all observed phenomena. Nevertheless, the work cited in this review suggests that the tendency of self-association among the fatty acids can help lead to a more integrated understanding of the role that fatty acids play in such systems.

On the topic of pitch deposition, concepts related to self-association of fatty acid groups help explain, first of all, why the pK_a values of fatty acids, when measured in the absence of salt and at sufficiently high concentration to lead to micelle formation, are two or three pH units higher than such acids as acetic acid, depending on experimental details. Suppression of dissociation within condensed layers of fatty acids can explain situations in which the fatty acids are sometimes released in a chaotic fashion when the pH momentarily exceeds a hard-to-predict critical value. Once such monolayer film structures are broken, the freed-up fatty acid soap molecules are susceptible to interaction with divalent metal ions, such as Ca^{2+} , often leading to deposit problems. Alternatively, when fatty acid soap layers are present at the water surface or at the surfaces of foam bubbles, wave action at solids surfaces or breakage of foam can lead to crumpling or folding of the monolayers, which provides a mechanism for generation of thicker and even macroscopic particles of tacky pitch.

Similar considerations help to explain the fussy nature of fatty acids with respect to trying to make them function as a hydrophobic sizing agent for paper. Evidence suggests that the aluminum ion – which papermakers usually rely upon when attempting to develop hydrophobicity with soap materials – do not interact strongly with fatty acids under papermaking conditions. This is possibly due to the manner in which the carboxylic acid head-groups are held close together in monomolecular films. In addition, the colloidal pK_a effect means that the pK_a values of the fatty acids may be outside of the range in which the aluminum species will have a cationic charge. It is possible, as an alternative approach, to generate hydrophobicity on surfaces that have been rendered cationic, followed by self-assembly of fatty acid soap molecules onto those surfaces. But such a strategy has so far failed to become popular among paper technologists.

Regardless of all the challenges associated with fatty acids present in papermaking systems, it remains true that fatty acids are relatively inexpensive, widely available, and environmentally friendly. Thus, there continues to be a strong motivation for papermakers to find a more valuable use for this material. Value-added uses for various extractive compounds would justify greater efforts at their removal before entering the papermaking system as a contaminant, where it tends to complicate efforts to deal with pitch deposition. For instance, the fatty acids could be used to hydrophobize surfaces pretreated by suitable cationic agents or metals having the right characteristics to serve as mordants for stable, well-oriented monomolecular films.

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