THE DETACKIFICATION OF STICKIES USING ELECTROHYDRAULIC DISCHARGE

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THE DETACKIFICATION OF STICKIES USING ELECTROHYDRAULIC DISCHARGE

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ABSTRACT

Stickies, synthetic or rubbery adhesives and coatings found in reclaimed paper, are still a major challenge after twenty-five years of paper industry recycling experience. Stickies negatively affect process efficiency and product quality in paper recycling more than any other type of contamination. Typical control strategies in recycle mills include screens and cleaners that remove stickies, and expensive chemical or mineral additives that pacify or detackify these polymers. However, the current state of technology has not solved the stickies problem.

A novel process has been developed based on electrohydraulic discharge (EHD) technology that detackifies and decreases the hydrophobicity of stickies. The process is based on the discharge of an underwater spark (50,000A, 5,000V, 150 μsec), which generates a shock wave, uv, hydroxyl radicals, and other oxidants. The technology is currently used to kill zebra mussels in water intake pipes at the Georgia-Pacific Plattsburgh, NY paper mill. The capital cost of one EHD unit is $60K.

Polyacrylate and polyvinyl acetate (PVAc) films were placed on stainless steel coupons, paper, and board. Samples were placed in either a 130-liter or a 10-liter tank filled with water, whitewater, or pulp slurry, and studied under various recycle process conditions. Treated samples and controls were then measured for tack, surface energy, and surface chemical composition. The tack and hydrophobicity of the polyacrylate films decreased and the hydrophobicity of PVAc decreased after only a few discharges. X-ray Photoelectron Spectroscopy (XPS) analysis showed that both the polyacrylate and PVAc had significant increases in oxygen bonded to the surface. The pH of treated stickie surfaces decreased as well. EHD treatment also improved the screenability of polyacrylate suspensions.
The fundamentals of detackification by EHD were investigated and evidence is presented that free radicals, generated by the ultrasonic shock wave, are available to react on the stickie surface. The XPS results indicate the mechanism involves oxidation of the polymer surface. Further experimentation demonstrated that UV and the pressure from the shock wave do not contribute to detackification.

Finally, a mill trial was conducted at VISY Paper in Conyers, Georgia, which is an 850 tpd 100% recycled linerboard mill. The mill wanted to reduce costs associated with cleaning stickies from dryer felts. The submersible EHD unit was placed in the stuff box of the top ply to treat the contaminated fiber. The tack of the mill stickies decreased over the treatment period and the time to clean the felts was decreased. Another trial is planned at Augusta Newsprint at the end of July 2000. EHD detackification is presently patent pending by the author of this dissertation, Howard Corcoran, and his PhD advisor, Sujit Banerjee, and has been commercialized by Sparktecc Environmental.
This Ph.D. Dissertation is dedicated to two of the most important people in my life, my late Grandfather, Howard V. Corcoran Sr., who has provided me with an invaluable education in life and my wife, Sara Guerrero Corcoran, who has loved and supported me through some great and sometimes trying times. We've made it!
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CHAPTER I. BACKGROUND

Chapter I provides the background on stickies, reviews current stickie control methods, and identifies specific problematic stickies and their properties that aid in evading removal and cause tack related problems. The fundamentals of tack are detailed in order to develop novel stickie control strategies. Additionally, several established methods of polymer surface modification are reviewed as potential means to alter the tack of stickie polymers. Sonochemical cavitation is one such means of generating free radicals that could oxidize stickie surfaces. Finally, a novel aqueous cavitation process is introduced, which may enable sonochemical modification of stickie surfaces in order to reduce or eliminate tack.

1.1 Introduction

Bergstrom\textsuperscript{1} stated in 1978, "the most insidious and fastest growing cause of contamination in paper recycling is synthetic or robbery adhesives and coatings, generally referred to as stickies in the paper industry. These stickies affect process efficiency and product quality in paper recycling more than any other type of contamination." More recently, Cauchon\textsuperscript{2} reported in 1997 that four out of seven U.S. recycling mills that were opened since 1994 had closed, citing the mills' inability to remove stickies from the recycled waste paper as the main reason for closure. A 1999 survey from Progress in Paper Recycling revealed that stickies, strength properties, and ink removal were the three major concerns of recycled paper manufacturers\textsuperscript{3}.

Additionally, the current joint Department of Energy (DOE) and Paper Industry Agenda 2020 is seeking new solutions for the elimination of stickies from recycled paper in order to reach the U.S. Government goal of 50% recycled fiber utilization\textsuperscript{4}. In sum, stickies are still a major challenge after more than 20 years of paper industry recycling.
experience, and very little recent progress has been made to develop new treatment methods to combat stickies. Stickies are a major bottleneck preventing further usage of recycled fiber, thus there is a pressing need for new technology that is affordable and safe to effectively eradicate or pacify stickies from recycled fiber pulp.

1.2 Stickies

Recycled papers are often contaminated with self adhesive labels and tapes, decals, stickers, waxes, inks, latexes, wet strength resins, binders, and other types of residues, which need to be removed during the recycle process. Adhesive contaminants are referred to as stickies because of their tackiness, which is the ability of a material to adhere to a surface with minimal applied pressure. The tacky nature of stickie particles cause them to agglomerate on various surfaces of the paper machine and build up into deposits, which can detach as larger stickie particles and cause sheet breaks, paper spots and holes, machine roll jams, or paper machine clothing destruction. The American Forest & Paper Association (AF&PA) has estimated that stickies cost U.S. recycled paper makers over $650 million a year. Individual mills have been reported to spend upwards of $700,000 on stickie control chemicals.

The best stock preparation process can only remove 99% of the contaminants, of which the remaining 1% is usually adhesives with specific gravities close to pulp slurries and a size typically from 10μm to 150μm in effective diameter. The most common processes to remove stickies in a recycle mill’s stock prep are pressure screens and cleaners. Pressure screens separate contaminants from fiber based on size. Coarse screens remove particles larger than about 1.55mm, while fine screens can remove particles larger than 100μm, however smaller stickies are accepted with the pulp. Smaller screen sizes can eliminate more stickies, but this will also increase the amount of
fiber rejected. Cleaners separate stickies from fiber based on the bulk property of density. Stickies with specific gravities in the same range as pulp slurries, 0.95 to 1.05, will be accepted with the pulp\textsuperscript{17,18}. Therefore, the problematic stickies are less than 100\mu m in diameter and 0.95 to 1.5 in specific gravity.

High temperature or pressure dispersion is used to break up contaminants into smaller particles so that they are practically invisible in the final product\textsuperscript{18}. Dispersed stickies can later deposit onto machine surfaces. Washing and flotation have also been included as other mechanical means of stickie removal\textsuperscript{18}, however, hydrophobic stickies will not usually be associated with wash water\textsuperscript{19} and flotation has been shown to be optimal for stickies larger than 400\mu m , which is within the range of fine screening\textsuperscript{20}.

Chemical strategies have been developed for stickies that modify the bulk properties that allow stickies to evade cleaners and screens. Talc and cationic polymers are among the most popular additives, but mixed results have been reported. An immediate drawback to chemical control is that additives are nonspecific to stickies and must be constantly added to the pulp regardless of stickie concentration, thereby lowering the efficiency and increasing the cost.

Talc is used to pacify stickies by covering the stickie surfaces, making them less tacky, and increasing their specific gravity, thereby making them easier to remove with cleaners\textsuperscript{21}. The downside of talc use is that it can interrupt fiber-fiber hydrogen bonding, effectively weakening the sheet. Talc also is found in machine deposits\textsuperscript{22}. Another common stickie control additive is a cationic polymer, usually DADMAC\textsuperscript{23}. Cationic polymers can be used to agglomerate stickies and aid in removal during screening. Anionic trash in the system is also attracted to cationic polymers, which could lower the stickie agglomeration or fixation efficiency\textsuperscript{24}.

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Table 1. List of common stickie contaminants found in recovered paper\textsuperscript{15}.

There are numerous types of stickie contaminants found in recovered paper (Table 1), however, only a few types of stickies are consistently found in machine deposits and final accepts pulp from the cleaners. Several analytical studies of stickies found in machine deposits and sheet specs\textsuperscript{25}, in pulp after the final screen accepts\textsuperscript{11}, and in pulp at the headbox approach\textsuperscript{26} reveal that the two major components are mixtures of polyacrylates and polyvinyl acetate, PVAc. Polyacrylates are commonly used as pressure sensitive adhesives (PSAs) for self-adhesive labels, tapes, stamps, and “Post It Notes”\textsuperscript{27}. Polyvinyl acetate is used as a watertight coating for board, book and ink binders, Elmers\textsuperscript{TM} brand glue, and as an additive to some PSAs\textsuperscript{17}. Figure 1 shows the general form for both polyacrylate and PVAc.
Figure 1. The general formulas for polyacrylates and polyvinyl acetate\textsuperscript{28}.

Polyacrylates and polyvinyl acetate evade most common stickie control strategies because of their bulk and surface properties. First, any stickie smaller than the fine screen size will be accepted. Second, the glass transition temperatures for both polyacrylate, \(-50^\circ\text{C}\)\textsuperscript{29}, and polyvinyl acetate, \(30^\circ\text{C}\)\textsuperscript{29}, are lower than typical recycle process temperatures, \(>40^\circ\text{C}\)\textsuperscript{30}. Since the polymers have chain mobility at process temperatures, under shear forces they can deform and pass through smaller fine screen openings. Additionally, the specific gravities of both polyacrylate and polyvinyl acetate are between 0.90 and 1.10\textsuperscript{31}, which is close enough to the density of pulp slurry, 1.0, to
allow them to be accepted with the pulp in cleaners. Polyacrylates and PVAc are both hydrophobic and usually nonionic, which prevents effective washing and makes charged chemical control difficult.

It is the combination of the aforementioned bulk and surface properties that allow polyacrylate and PVAc to escape all known mechanical and chemical controls. Similarly, it is the same bulk and surface properties of these polymers that are responsible for tack. The tacky nature of these mixtures results in machine deposition, runnability problems, and product quality issues. Therefore, it is critical to have a fundamental understanding of the mechanism for tack in order to develop novel, more effective stickie control strategies.

1.3 Tack Theory

Regardless of the chemical nature of the stickie, it is the property of tack that interferes with machine runnability and paper quality\(^9\). Tack is the stickiness of an object, qualitatively determined by touch. For example, one places a finger on the adhesive backing of piece of tape. The piece of tape is then bound to the finger and requires the use of force to remove the piece of tape from the finger. More specifically, tack is the energy required to separate two objects not permanently bound together\(^{32}\), in this case, the finger and the adhesive tape. Tack can be quantified, usually by measuring the force of separating a metal probe\(^{33}\), which replaces the finger, from an adhesive surface. Tack is essentially an adhesion mechanism where one surface immediately binds to another.

The first requirement for an adhesive to be tacky is that it is compliant, meaning deformable\(^{34,35}\). This compliance allows for intimate contact with another surface, the adherend. The second requirement is that the adhesive has sufficiently less surface
energy than the adherend in order to dissipate the excess energy; in other words, it must wet the surface\(^{34}\). This adhesional wetting decreases the adherend-air interface, forming a bound interface between the two. The adhesive is more attracted to the adherend than it is to itself. Thermodynamically, the interfacial energy of the combined adhesive-adherend is more favorable than the surface energies of the individual surfaces in air. Essentially, a higher energy surface is replaced with a lowered energy interface. Upon removal of the adherend, the viscoelastic adhesive will stretch without breaking, dissipating the applied energy of separation, until the bond is broken.

The first requirement, compliance, of adhesive tack is dependent on the bulk properties of the material\(^{35}\). In the case of polymers the compliance or softness is dependent upon the glass transition temperature, \(T_g\). Polymers are more compliant above their \(T_g\). In the case of 2-ethylhexyl acrylate, a common polyacrylate that is tacky at 25\(^\circ\)C, the \(T_g\) is about \(-50^\circ\)C\(^{29}\). PVA is a solid at 25\(^\circ\)C. It does not become tacky until it passes through its glass transition around 30\(^\circ\)C\(^{29}\), thus both polyacrylate and PVA are tacky in most recycled processes (usually \(>40^\circ\)C).

The second requirement\(^{38}\), wetting, is governed by the Young equation shown in Equation 1\(^{36}\):

\[
\gamma_{LA} \cos \theta = \gamma_{SA} - \gamma_{SL}
\]  

(1)

The Young equation relates the adhesive contact angle \(\theta\) to the surface energies of the adhesive, \(\gamma_{LA}\), and solid adherend, \(\gamma_{SA}\), and the interfacial energy, \(\gamma_{SL}\) (Figure 2). In this case the subscript S is the solid adherend, L is the liquid adhesive, and A is air. Wetting occurs if \(\gamma_{LA}\) is sufficiently less than \(\gamma_{SA}\), such that the reduction in surface energy is thermo-dynamically favored. Descriptively, the adhesive contact angle \(\theta\) will be 0 degrees for complete wetting, 180 degrees for nonwetting conditions, and in between 0
and 180 degrees for partial wetting\textsuperscript{35}. The closer the angle is to zero degrees the better the wetting.

\[ \gamma_{SA} = \text{Interfacial tension between adhesive and adherend} \]

\[ \gamma_{LA} = \text{Surface tension of adherend} \]

\[ \gamma_{LA} = \text{Surface tension of adhesive} \]

\[ \cos \theta = \frac{\gamma_{SA} - \gamma_{LA}}{\gamma_{LA}} \]

**Figure 2. An adhesive liquid on the surface of an adherend\textsuperscript{15}**.

There are many materials that only fulfill one of the requirements of tack and thus are not sticky. Teflon, which is valued for its resistance to sticking, has a very low surface energy; however, it does not fulfill the first requirement of tack, for it is a solid, which prevents intimate contact with other objects\textsuperscript{37}. In contrast, liquid Teflon, which is used as a lubricant, is very tacky because it is both soft and of low surface energy\textsuperscript{38}. Additionally, silicon resins are compliable and soft, but have negligible adhesional tack, because of their higher surface energy\textsuperscript{39}.

The surface energy difference between two surfaces is the driving force for adhesive tack. Surface energy is the amount of work required to increase the area of a surface by a unit amount\textsuperscript{36}. Attractive forces hold liquids together; thus, a greater force than those holding the liquid together must be employed to change the surface area. Solids also have surface energies due to attractive molecular forces, however, the bulk is held together primarily with covalent or metal bonds. The short-range intermolecular
forces responsible for the surface energy include the universal London dispersion forces and may also include hydrogen and metal bonding.

Figure 3. Attractive forces between molecules at the surface and interior of a liquid\textsuperscript{36}.

Figure 3 shows an example liquid where the bulk molecules are, on average, subjected to equal forces of attractions in all directions\textsuperscript{36}. In contrast to the bulk, the molecules at the air-liquid interface experience unbalanced attractive forces pulling those molecules from the surface toward the interior, constantly replacing the surface molecules with ones from the bulk\textsuperscript{36}. Viscoelastic adhesives have much lower molecular mobility than liquids, thus, this bulk surface reordering takes place on the range of months. In the case of solids, the molecules are fixed at the surface and experience the same unbalanced, attractive forces at all times. Essentially, all liquid and solid surfaces are attractive due to these unbalanced forces; however, most surfaces do not meet the first requirement of tack, which is that the surface is able to have intimate contact with another surface. Most solid surfaces are too rough to accomplish this intimate contact\textsuperscript{36}.

According to Fowkes\textsuperscript{39} the surface energy can be expressed as the sum of the parts of all of the molecular interactions, given by equation 2:

$$\gamma = \gamma^d + \gamma^f + \gamma^p + \gamma^s + \gamma^m + \gamma^a + \gamma^t$$  \hspace{1cm} (2)
where \( d \) refers to London dispersion forces, \( i \) to induced dipole-dipole, \( p \) to dipole-dipole, \( h \) to hydrogen bonding, \( \pi \) to \( \pi \) bonding, \( a \) to acceptor-donor (acid-base), \( m \) to metal bonds, and \( e \) to electrostatic interactions. While dispersion forces are universal, the other interactions will depend upon the property of the material. To further simplify equation 2, the contributions have been narrowed down to two, the dispersion forces, \( \gamma^d \), and the nondispersion forces, the sum all of the other potential interactions, \( \gamma^n \), which are commonly referred to as polar forces. The simplified version of the total surface energy is shown in equation 3:

\[
\gamma = \gamma^d + \gamma^n
\]  

(3)

It is now apparent that by increasing any of these components, for example by bonding oxygen to the surface, the surface energy will increase, which will decrease tack. Israelachvili gives a more detailed examination of intermolecular and surface forces and adhesion.

A thermodynamic description of tack adhesion is given by the work of adhesion. The work of adhesion, \( W_s \), is simply the amount of energy required to separate two adhered surfaces. If the \( W_s \) is positive, there is adhesion. The work of adhesion is the sum of the surface energies of the adhesive and adherend in air minus the surface interfacial energy of the combined adhesive and adherend and is given as the Dupre equation 4:

\[
W_s = \gamma_{LA} + \gamma_{SA} - \gamma_{SL}
\]  

(4)

Figure 4 shows schematically the work of adhesion, where \( A \) represents an adhesive and \( B \) represents a solid adherend.
Figure 4. Schematic of the work of adhesion\textsuperscript{42}.

The work of adhesion can also be stated as the negative change in Gibbs Free Energy divided by the surface area, an alternative Dupre equation given in equation \textsuperscript{5}:

\[
W_a = -\Delta G/A
\]  

(5)

However, equations 4 or 5 can only qualitatively predict whether or not adhesion can occur, since the interfacial energy can only be measured indirectly\textsuperscript{41}. In most cases adhesion occurs if the adherend surface energy is higher than that of the adhesive\textsuperscript{35,63}. In the case of PSA adhesive bonding, the adhesive surface energy \textit{has} contributions from both dispersion forces and polar interactions. When an adherend is brought into contact with the adhesive, the strongly attractive surface forces of the adherend induce the surface molecules of the adhesive from an attracted state to a repulsive state, which allows the adhesive to immediately wet the adherend surface. The surface forces of the adhesive are now more attracted to the adherend than they are to themselves\textsuperscript{41}.

The bonds between an acrylic adhesive, an acrylate, and a stainless steel adherend are the result of van der Waals bonds of both the adhesive and metal, the polar forces of the adhesive, and the metal bonds of the steel. In this case, the metal bonds provide the excess surface energy that drives adhesion, which results in the van der Waals forces of the adhesive to become immediately attracted to the surface of the metal. This attraction
leads to the surfaces quickly bonding together, which is essentially tack. The surface energy of stainless steel is around 45 dynes/cm\(^2\), while the surface energy of most polyacrylates is from 20 to 25 dynes/cm\(^2\). Polyvinyl acetate has a surface energy around 36 dynes/cm\(^2\). Both polymers have high tack values above their glass transition temperatures.

Zosel\(^4\) has provided empirical evidence supporting higher tack values for adhesives with much lower surface energies than an adherend probe. Zosel has found very few published empirical results concerning the relationship between tack and surface energy, despite that most theories of adhesion are dependent upon this relationship. Both Sherriff\(^5\) and Counsell\(^6\) found an increase in tack force with increasing adherend surface energies adding further support for the role of surface energy in tack.

The last step in adhesion, the debonding stage, is the separation of the adhesive from the adherend. This is desirable with self-stick adhesives like those on name labels and "Post It Notes"\(^7\). The amount of work required to separate the adhesive from the adherend can be estimated from work of adhesion equation 4; however, experimental results give values at least three orders of magnitude higher\(^4,5\). This discrepancy is explained by the viscoelastic nature of the polymer adhesive, which is not considered in the work of adhesion equations 4 or 5\(^7\). The adhesive is able to initially perform like a liquid as it wets the surface of the adherend. Upon high shear strain rates like those encountered during removal, the adhesive is able to behave elastically, resisting separation. The adhesive has cohesive strength due to molecular interactions and chain entanglement, and the adhesive has the ability to dissipate the energy of separation into the deformation of the polymer. The deformation is the stretching of the material until
failure at the interface occurs. Thus, the viscoelastic adhesive has over 1000 times more strength than the separation force predicted solely on the original surface energy adhesional forces using equation 467.

Stickies also tend to be attracted to other stickies in water, which is known as hydrophobic, literally “water hating”, interaction. Water has a strong inclination to hydrogen bond to itself. Non-polar molecules, such as polyaacrylates with hydrocarbon groups, are incapable of forming hydrogen bonds with water and are considered hydrophobic for this reason41. The attraction of hydrophobic materials in water is around five times greater than in air41. This increase in attraction is actually due to the fact that the water’s relatively stronger hydrogen bonds need to be broken in order to form relatively weaker van der Waals bonds with the hydrophobic material, which is thermodynamically unfavorable.

In summary, a tacky polymer must possess surface energy that is sufficiently lower than an adherend, which is a property of the surface. A tacky polymer must also possess the right balance between softness and the ability to dissipate energy, which are both properties of the bulk47. This illustrates the importance of both bulk and surface properties in tack. Changing the bulk properties, such as raising glass transition temperature can alter tack. Similarly, changing the surface structure can be used to reduce or eliminate the tackiness, for example, by raising the surface energy48. Also, if stickie surfaces could be made more hydrophilic, there would be less of a hydrophobic attraction for other stickie contaminants, which could reduce deposits. Polymer research offers many established techniques to modify stickie surfaces in order to potentially diminish the problem of tack in recycled paper manufacture.
1.4 Surface Modification of Polymer Surfaces

Many methods have been developed in polymer science to change the surface characteristics of polymers in order to reach a desired surface property, such as increasing the surface energy of plastics by oxidation\textsuperscript{41}. These methods of surface modification may be useful in pacification of stickies in recycled pulp slurries. What follows is an overview of several methods of polymer surface modification—some may be potentially useful to recycled paper manufacture. Further analysis of potential methods of stickie detackification by surface modification is explored in Chapter 2.

Polymer surface modification was first considered during the 1950s, when low density polyethylene (PE) film was being used as a heat sealable packaging material\textsuperscript{49}. The PE film was difficult to print on with available inks, which were also of low surface energy, making adhesion difficult\textsuperscript{69}. The inks could not wet the PE surface. Also, PE had no acid-base functionality, as it only contained hydrocarbons. Thus, empirical pretreatments, such as corona discharge, were developed to increase the surface energy of polymer films\textsuperscript{69}. Several methods, such as corona and flame, which oxidized the surfaces, inert and active gas plasma treatment which cross-linked and added functional groups, and plasma deposition which created a cross-linked thin polymer coating on the surface, have been developed to modify plastic surfaces\textsuperscript{48-51}. The formation of the hydroxyl radical by corona or flame treatment leads to the oxidation of the polymer surface\textsuperscript{49}. Figure 5 shows the reaction of a methyl side chain of a polyisobutene with a hydroxyl radical, which is the result of corona or flame treatments. The reaction pathway results in the formation of formyl and carboxyl groups on the polymer, which change the polymer's functionality\textsuperscript{49}. This oxidation results in higher surface energy and lowered hydrophobicity\textsuperscript{49}.

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Chtourou et al.\textsuperscript{50} have oxidized PE fibers with ozone and fluorinated gases in order to give PE fibers carboxyl and aldehyde functionality, which will enable the fibers to hydrogen bond with wood fiber. Sakata et al.\textsuperscript{51} have oxidized wood surfaces for improved adhesion of veneers using corona treatments. They found that while aldehyde content increased, carboxylic acid content remained constant. Geiss et al.\textsuperscript{52} have selectively uv-crosslinked pressure sensitive adhesive film surfaces in order to increase peel strength in certain areas by increasing cohesive strength, which also decreased the tack. Ultraviolet exposure breaks carbon to hydrogen bonds, which allows for bonding of different polymer chains. The unexposed areas maintained their tackiness to achieve some initial stick. Figure 6 shows the cross-linking reaction product of two polymer chains that have been subjected to uv energy.

Several US patents have been granted based on the surface modification of polymers. Arbit\textsuperscript{53} has a patent for the enhanced wettability of organic surfaces.

Basically, a hydrophobic surface becomes more hydrophilic after being oxidized in gas
plasma. Arbit's patent is a broader version of the Gesser et al.\textsuperscript{54} patent, which protects the application of changing the surface of a contact lens from hydrophobic to hydrophilic. In this case, the contact lens is wettable by human tears, which helps to hold the lens on the eye\textsuperscript{54}.

![Chemical structure diagram](image)

Figure 6. The crosslinking of two polymer chains due to exposure to uv radiation\textsuperscript{57}.

It is necessary to point out that most of the methods mentioned above are for improved adhesion, which is achieved by raising the surface energy and increasing the functionality. The surfaces in every case are not becoming tacky; they are becoming better adherend substrates. All of the surface modifications mentioned here have been carried out in the presence of various gases or at vacuum. If oxidative modification of stickies is possible, the process will need to be carried out in aqueous slurry. Sonochemistry provides a means of creating free radicals in water, which could oxidize stickies in pulp slurry.
1.5 Sonochemistry

Sonochemistry is the study and application of acoustical oxidative reactions in liquids. Sonochemistry is mainly concerned with chemical reactions that result from cavitation, which is the formation of gas-vapor bubbles as an acoustical shock wave passes through liquid, such as water. What follows is a physical description and possible sources of cavitation. Then, the chemistry of cavitation is reviewed and related to sonochemical polymer modification, which is explored as a potential method of stickie surface modification.

Cavitation bubbles are generated during the rarefaction or negative pressure phase of the acoustical wave and implode rapidly after formation. Figure 7 shows the compression and rarefactions portions of the acoustical pressure wave, as they relate to the pressure amplitude.

![Pressure (P) graph.](image)

Figure 7. An acoustical wave as it relates to the pressure (P) amplitude, where c is compression portion and r is the rarefaction portion.
The main requirement for sonochemical cavitation reactions is the presence of dissolved gas, usually oxygen\textsuperscript{56}. Cavitation bubbles often reach diameters from 1\textmu m to 100\textmu m and have an average maximum lifetime of 400\textmu s\textsuperscript{57}. Figure 8 shows a cavitation bubble that is in a state of compressive collapse at a metal surface. The cavitation process is shown in Figure 9, which illustrates the fate of a cavitation bubble. Before cavitation occurs, an initial positive pressure wave passes through the liquid, compressing the liquid and any undissolved gas. At this point, there is no cavitation. Cavitation begins when the trailing negative-pressure tail of the acoustical wave, known as the rarefaction phase, passes through trapped gas-vapor nuclei.

![A collapsing cavitation bubble on a metal surface](image)

Figure 8. A collapsing cavitation bubble on a metal surface\textsuperscript{58}.
Points A, B, and C lie in the rarefaction region of the acoustical wave. Point A in Figure 9 shows the original gas-vapor nucleus. The bubble then forms as the pressure drops below the vapor pressure of the water, represented by point B, until it reaches its maximum size at point C, which depends on the intensity of the wave. Points C through F represent the respectively decreasing sizes of the cavitation bubble, starting as the pressure wave begins to increase out of the rarefaction portion, continuing as the compression or positive pressure phase of the acoustical wave passes through the liquid. The acoustical wave exerts pressure on the cavitation bubble, shown as point C, until it is compressed through points D, E, and F. It is at point F that the bubble is undergoing collapse. This cycle repeats itself until the energy from the acoustical wave dissipates and the pressure is smaller than the vapor pressure of water.
The source of sonochemical cavitation can be either ultrasonic or electrohydraulic discharge, both of which can produce high-pressure acoustical waves. Regardless of acoustical source, the main requirement for cavitation to occur is that the pressure from the acoustical wave, \( P_a \), must be higher than the difference of the nominal pressure, \( P_n \), and the vapor pressure, \( P_v \), of the liquid. Equation 6 shows the conditions necessary for liquids to cavitate.

\[
P_a > P_n - P_v
\]  

(6)

Figure 10 illustrates the response of a pre-existing gas-vapor nucleus or microbubble to a single cycle of acoustic pressure\(^9\). The bubble radius increases rapidly in magnitude over the negative, rarefaction portion of the acoustic cycle, followed by the collapse as the pressure begins to increase out of the rarefaction portion to the positive pressure portion\(^9\). The recorded temperature is the highest as the pressure increases from negative to positive.

Figure 10. Response of a cavitation bubble nucleus to a single acoustic cycle. The vertical scale plots are normalized values of the bubble radius and interior gas temperature; the equilibrium radius is 1\( \mu \)m; the equilibrium temperature is 293 K; a normalized time of 6.28 corresponds to a full acoustic period\(^9\).
In the process of the high-pressure bubble implosion, large amounts of energy are released during the collapse of the cavitation bubble, which is the foundation of sonochemistry. The high-energy implosion produces free radicals by splitting water into hydroxyl and hydrogen radicals, which is known as homolysis. These radicals have been identified using electron-spin-resonance spectroscopy. To a lesser extent, peroxide radicals are formed. However, hydroxyl radicals initiate all further sonochemical reactions. The decomposition of water, which is the result of cavitation, results in the following reactions:

\[
\begin{align*}
\text{H}_2\text{O} & \rightarrow \text{HO}^- + \text{H}^+ \\
\text{H}^+ + \text{O}_2 & \rightarrow \text{HO}_2^-
\end{align*}
\]

\[
\begin{align*}
\text{HO}_2^- + \text{HO}_2^- & \rightarrow \text{H}_2\text{O}_2 + \text{O}_2 \\
\text{HO}^- + \text{HO}^- & \rightarrow \text{H}_2\text{O}_2
\end{align*}
\]

There are three zones that can be used to describe a collapsing cavitation bubble shown in Figure 11. Zone 1 is the gaseous vapor region of the cavitation bubble, where the temperatures upon bubble collapse can be in excess of 5,000K. Zone 2 is the gas-liquid transition region, or interface. The temperatures in Zone 2 can reach temperatures up to 1900K. Zone 3 is the bulk liquid, which is at ambient temperature. Figure 12 shows the temperature gradient between Zone 1 and Zone 3 in relation to the collapsing cavitation bubble, which can be recognized as a localized hot spot due to the high temperatures generated upon collapse of the cavitation bubble.
Figure 11. The three reaction zones for sonochemical reactions from a collapsing cavitation bubble\(^6\).

Symmetric collapse

Figure 12. Collapse of a cavitation bubble showing localized hot spot\(^6\).

There are many potential sites of sonochemical reactions initiated by cavitation, which are illustrated in Figure 13. In a homogeneous liquid medium, such as water, the
three zones of the collapsing cavitation bubble are potential reaction sites. The main reaction site in a cavitation bubble in water is at the liquid-gas vapor interface. Although the temperature of the vapor phase is much greater than the temperature of the interface, up to 5,000K compared to 1,900K, the liquid-gas vapor interface has a greater concentration of water that can undergo homolysis, which results in a greater concentration of hydroxyl radicals. There is evidence that hydroxyl radical formation occurs in all three zones to some extent. Zone 3, which represents the bulk surrounding the cavitation bubble, was shown to contain only about 10% of the hydroxyl radicals generated upon collapse of the cavitation bubble. Stickies that are within the region of the collapse of the cavitation bubble could be oxidized by the resultant free radicals.

Cavitation bubbles also occur at nucleation sites on solid surfaces, which is also illustrated in Figure 13. Upon collapse of the cavitation bubble, free radicals are produced that can directly react with the solid surface. Since most solids in a liquid medium, such as water, have entrained air on the surface and in pores, conditions for cavitation to occur at the surface are present. Thus, cavitation bubbles close to stickie surfaces and cavitation bubbles that form directly on stickie surfaces could be likely mechanisms of free radical initiated surface modification. The two other mechanisms, surface cleaning and emulsification, shown in Figure 13 relate to mechanical modification, not sonochemical reaction mechanisms.

Sonochemical modification of polymers has been of recent interest because of the possibility of wet chemical reactions. Both polymerization and polymer modification are possible under sonochemical treatment. The potential mechanisms are cavitation reactions and high-pressure shearing of the surface. However, there is evidence that
Figure 13. Possible sites of reaction induced by cavitation\textsuperscript{62}.

cavitation is the source of polymer modification. For example, it has been demonstrated that polymer modification does not occur in the presence of high-pressure acoustical waves without gas nuclei because sonochemical reactions require gaseous cavitation\textsuperscript{55}. If the pressure did break bonds, then some degradation of the polymer should have been reported. It has also been reported that free radical polymerization can be carried out using cavitation\textsuperscript{55}. Free radicals produced from sonochemical cavitation are also capable
of breaking C-C, C-H, and C-O bonds. One outcome is that hydroxyl radicals generated from cavitation can combine with the polymer surface. In addition to oxidation, broken bonds can result in the crosslinking of existing polymer chains or the grafting of monomers to the polymer backbone. Figure 14 shows the hydroxyl radical initiated oxidation of 2-hydroxyterephthalate, which is commonly used to show oxidation potential. Cavitation generated hydroxyl radicals have also played a role in increasing the yields of reactions, such as the oxidation of arylalkanes shown in Figure 15, which has an increase in yield from 27% to 73%.

![Figure 14. The hydroxyl radical initiated oxidation of 2-hydroxyterephthalate.](image)

![Figure 15. The oxidation of arylalkane in water with KMnO₄.](image)
The presence of hydroxyl radicals does not always lead to incorporation of oxygen at the surface. For example, sonochemical reactions can also lead to the formation of conjugated carbon double bonds, which are initiated by hydroxyl radicals\textsuperscript{63}. Figure 16 shows an example of the reaction of polyvinyl fluoride with NaOH in water, which leads to the formation of conjugated carbon bonds. The four wavy lines under the reaction direction signify ultrasonic treatment and hydroxyl radical formation.

![Reaction Diagram]

Figure 16. The reaction of polyvinyl fluoride with NaOH in water\textsuperscript{63}.

In summary, both ultrasound and electrohydraulic discharge (EHD) are sources of sonochemical cavitation. Ultrasonic sonochemical cavitation has been shown to oxidize and crosslink stickie surfaces\textsuperscript{55,65}. While ultrasound is generally used as a source of sonochemical cavitation in laboratory studies, industrial scale applications are limited by high capital and operations costs\textsuperscript{66}. The following section explores the capabilities and applications of a commercially available EHD device, which is an alternative low capital cost device to generate free radicals.

\textbf{1.6 Electrohydraulic Discharge}

Electrohydraulic discharge treatment is a potential method for modifying adhesive surfaces in an aqueous solution. It is essentially a very powerful underwater spark plug. The underwater discharge generates ultraviolet radiation, uv, and a plasma channel which contains radicals and ozone. In addition, the plasma channel pressure generates a shock wave that propagates through the water and results in cavitation. As stated in the previous section, cavitation creates free radicals, like hydroxyls, which oxidize and
crosslink polymer surfaces. EHD has many widely used applications such as biological control.

EHD is based on the discharge of energy into an aqueous solution through a plasma channel formed by a high current (>50,000 Amps) and a high voltage (>5,000 Volts) electrical discharge between two submerged electrodes, which lasts 150-300 μs. Plasma is a state of matter in which most of the atoms are ionized, making them electrically conductive. Plasma can be created in water by applying an extremely high electrical field, called field ionization, which dislodges electrons from oxygen and hydrogen atoms. This dislodging is called water splitting. Each EHD results in the production of 3-4 ml of plasma. More importantly though, the high-pressure plasma channel is the source of an acoustical shock wave that exerts enough pressure on the surrounding water to create cavitation, through larger volumes of water than the plasma channel. The resultant free radical chemistry of cavitation due to acoustical shock waves will be studied as a means to detackify stickies in water.

The EHD discharge event is very short and sharp. The pressure developed in open water 30cm from the plasma channel can reach up to 270 atm depending on the discharge energy, and has a speed of propagation of about 1500m/s. Robinson et al. have described the components and energy of an electro-hydraulic discharge. They have determined that the main output of energy is in the plasma column, which generates the shock wave and ultraviolet light (UV). Figure 17 shows the plasma column between the two electrodes, which are typically 4.2mm apart. The ultraviolet radiance was measured using a monochromator coupled with a photomultiplier. For a stored capacitor energy of 1500 J, 28% was converted to UV radiation with the remaining 72% generating the plasma channel, which rapidly explodes, giving off more UV radiation and a shock wave.
Figure 17. The plasma channel generated between the electrodes during an electrolydraulic discharge\(^7\).

EHD is based on exploding wire research, which started in the 1940s, and has been used extensively by the U.S. Navy to detonate underwater mines, deep water sounding and sediment analysis, and by metal works for electro-discharge machining (EDM)\(^7\). A less powerful, 1 Hz discharge is used in medicine, called lithotripsy, to dissolve kidney stones\(^9\). The main mechanism of kidney stone disintegration is believed to be mechanical, not sonochemical\(^9\). However, the acoustic field generated by lithotripsy results in cavitation\(^9\). An acoustic waveform from a lithotripter is shown in Figure 18. The maximum pressure generated by the lithotripter acoustic wave shown in Figure 18 is 15atm and the maximum negative pressure is 3 atm\(^9\), where the y axis represents the pressure amplitude and the x axis represents the time. Figure 19 illustrates...
the resultant cavitation of the lithotripter for a single shock (a) and for ten shocks (b) in water. The white bars in Figure 19 represent the focusing aperture, which measures 15.4cm\textsuperscript{59}. The light-spots in Figure 19 represent photons emitted by the cavitation, which represent temperatures of at least 1000K\textsuperscript{59}.

![Image](image_url)

**Figure 18.** An acoustical waveform for a shock wave generated by a lithotripter\textsuperscript{59}.

The lithotripter is a source of EHD initiated cavitation and is used in small volumes. An EHD device from Sparktec Environmental, Canada, is a source of underwater acoustical waves for larger volumes. The shock wave for the Sparktec EHD device has been recorded by Welsh and is shown in Figure 20\textsuperscript{71}, where 40psi converts to 2.7atm. There are similarities in the acoustical wave that results from EHD and from a lithotripter, which was shown in Figures 18 and 20. The only difference between the lithotripter and the Sparktec EHD unit is the scale; the mechanism, i.e. sonochemical cavitation, is the same. Welsh also measured the frequency of the acoustical pressure wave, which is shown in Figure 21\textsuperscript{71}.
Figure 19. The luminescence of cavitation bubbles produced by a lithotripter for 1 shock (a) and for 10 shocks (b)\textsuperscript{79}.

Rock fragmentation and water purification have been studied, and provide varying results\textsuperscript{80}. Rock fragmentation is the result of the high pressure from the shock wave, whereas the free radicals and ozone generated from the shock wave and UV are potentially available to oxidize contaminants in waste water. The problem with water purification is that ozone is only generated in the small plasma channel (3-4 ml), requiring a large number of discharges to purify a small volume of water\textsuperscript{79}. The free radicals generated by the EHD shock wave cavitation are significant, but not enough to sterilize waste water\textsuperscript{73}. 

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Other applications of EHD have been to control the settlement of zebra mussels on water intake pipes and to limit biofilm formation. Zebra mussels build up on protective intake pipe screens to the point where water can no longer be pumped to the receiving area. Biofilm causes similar problems to that of stickies with the usual addition of bad odors. Mackie et al.\textsuperscript{74} has shown that EHD treatment of pipes reduces zebra mussel build-up, with about 100X less zebra mussels depositing on pipes that were pulsed.
EHD was also shown to increase zebra mussel mortality by crushing the shells of the mussels. Discharging up to 200 meters from the water intake screens is still an effective method of mussel control. Biofilm formation was also reduced, however, discharging did little to remove settled biofilm. In both cases it is hypothesized that the mechanism of prevention is the pressure from the shock wave. The only pulp and paper application to date using EHD for any reason is Georgia Pacific Plattsburgh, which uses an EHD unit to successfully prevent zebra mussel build-up on water intake pipes from Lake Champlain.
CHAPTER 2. PROBLEM ANALYSIS

2.1 Development of the Problem Statement

There are four major points from the literature pertinent to the problem of stickies in recycled paper, and they follow:

1. Stickies are responsible for reduced paper quality, reduced paper machine runnability, and increased costs due to machine down time, as well as expensive control chemicals, and rejected rolls of paper.\textsuperscript{5,8-16}

2. Both polyacrylates and polyvinyl acetate, PVAc, are the most common types of stickies found in machine deposits due to their tacky nature at process temperatures and their ability to evade removal and conventional control processes.\textsuperscript{11,25,26}

3. Current stickie removal and control methods have provided neither a universal solution nor a stickie specific approach to elimination or passivation.\textsuperscript{17,18,20,26}

4. The tacky nature of a stickie is due to its low surface energy and deformability.\textsuperscript{28,34,35} Additionally, stickies in water adhere to other types of stickies and surfaces due to the hydrophobic effect.\textsuperscript{41} Detackifying stickies requires either raising the surface energy of the stickie, making the stickie less deformable, or making the stickie more hydrophilic.\textsuperscript{35,47}

First, stickies are a major challenge and cost to the recycled paper manufacturer and new process technology is needed to pacify or eliminate stickies in an economical manner. Such a technology could be a useful tool in increasing the amount of recycled paper produced as well as decreasing the associated costs.

It has been well established that polyacrylate and PVAc stickies evade current state-of-the-art removal and control techniques and comprise the majority of stickie
deposits found on paper machine surfaces\textsuperscript{11,25,26}. Therefore, it is essential to find a new control regime that specifically targets polyacrylate and PVAc. The current methods used to control stickies have weaknesses that are exploited by stickies. For example, separation using cleaners is poor due to the similar specific gravities of fiber, polyacrylate, and PVAc\textsuperscript{26}. Screens cannot remove stickies that are smaller than the screen size or deformable enough to pass through the holes\textsuperscript{17}. Also, stickies that are subjected to high pressure or temperature dispersion are still available to deposit onto paper machine surfaces. Chemical additives are expensive and can reduce paper quality. Moreover, control chemicals are not specific to stickies, leading to overloading the system with additives in order to raise the probability of contact, which results in increased costs and deposits.

It is clear from stickies literature that no universal solution to control stickie contaminants exists. Few attempts have been made to introduce new stickie control strategies, especially for polyacrylates and PVAc. Only two practical solutions have been recently advanced in the stickie literature. The first solution seeks to replace problematic stickies in adhesives and the second optimizes cleaner removal.

One potential solution is to start at the source, by replacing problematic adhesives, such as polyacrylates. The adhesives industry has been testing new types of adhesives that have more benign consequences in recycled paper streams, such as water-soluble polymers\textsuperscript{26}. The problem with water-soluble adhesives is they perform poorly in humid environments and have lower tack strength\textsuperscript{77}, which is a characteristic that is usually unacceptable to consumers.

The second approach is to optimize the present control methods to obtain better separation of polyacrylate or PVAc from fiber. For example, Wilhelm\textsuperscript{26} et al. has
Patented a cleaning process that takes advantage of the difference between the coefficients of thermal expansion of stickies and water\textsuperscript{26}. The process is accomplished by having two sets of cleaners in series with different temperatures. For example, a polyacrylate or PVAc that has a specific gravity of 1.0 in the first cleaner will have a different specific gravity in the second cleaner because of the higher temperature. Essentially, the stickie will become less dense at some higher temperature.

Any further gains from process or chemical optimization is highly unlikely, thus a new approach must be taken. One promising and underexplored area is to detackify stickies by exploiting the mechanism that makes stickies tacky in the first place. This has already been utilized to some extent by using talc and using dryer can coatings.

Stickies adhere to talc due to surface energy differences and hydrophobic interactions\textsuperscript{21}. For example, talc changes the surface energy of the stickie in order to detackify it. The problem is that talc usage is not stickie specific and can lead to deposits and poor paper quality. A more desirable way to control stickies is to raise the surface energy or minimize the hydrophobic interaction without chemical additives.

The opposite approach is to use lower surface energy materials on the paper machine, such as Teflon coated dryer cans\textsuperscript{79}. However, this is a highly improbable scenario given the need for affordable and durable equipment in the mill. The low surface energy of the Teflon prevents the adhesion of the low surface energy stickies\textsuperscript{78}. However, these coatings are expensive and are easily scratched, which can render them useless. Finally, Hassler\textsuperscript{79} et al. has introduced a process that provides a continuous coating of low surface energy polymer emulsion to the dryer can rolls, which reduces stickie build-up. This process is capital intensive and untested in North American paper mills. There is also a question about the effects of the emulsion surfactant on sizing and
print quality. Consequently, it is unlikely that the extensive use of low surface energy materials will be common in the future.

2.2 Problem Statement

It becomes apparent that a method to detrackify stickies by changing their surface properties without the use of chemical additives could be a beneficial control strategy. Thus, from an extensive review of the stickie literature and all of the current state-of-the-art stickie control methods and processes, the following problem statement has been developed:

There is a need for inexpensive and simple methods of detrackifying the most problematic stickies, polyacrylates and PVAc, by altering the surface properties of these stickie materials without the use of chemicals.

2.3 Analysis of Potential Solutions

A potential method of detrackifying stickies using sonochemical cavitation as a means to react with and oxidize stickie surfaces has emerged from the literature. Additionally, there exists an affordable and reliable means of pulsed underwater sonochemical cavitation. The following summarizes the main points regarding a potential method of detrackifying stickies.

1. Polymeric stickie surface modification is possible using many methods, including free radical oxidation and UV crosslinking. These modifications can lead to higher polymer surface energy and decreased hydrophobicity, which can contribute to lower tack.

2. Sonochemical cavitation results in the formation of highly reactive hydroxyl radicals that have been documented to combine with polymer surfaces. The potential
reactions are oxidation and crosslinking, which would decrease the tack of stickie surfaces and decrease its hydrophobic nature\textsuperscript{55,63}.

3. An electrohydraulic discharger (EHD) is a device that produces a pulsed acoustical shock wave, which results in cavitation and subsequent hydroxyl radical reactions\textsuperscript{65,70,71,72}. The EHD is designed to release a high voltage-high current discharge underwater\textsuperscript{74}.

In order to detackify stickies the method must increase the surface energy. One way to do this is to increase polar contribution to surface energy, which can be accomplished by bonding oxygen to the surface of the stickie. A source of this oxygen could be hydroxyl radicals from sonochemical cavitation. The surface energy increases as oxygen is bonded to the surface, and results in a decrease in tack. Oxygen has polar contributions that a hydrocarbon chain does not, which serves to increase the surface energy. A related benefit is that the oxygen on the surface of the stickie will be able to hydrogen bond with the water, thereby decreasing the hydrophobic interaction.

Surface energy is determined indirectly from the contact angle measurements of two or more liquids, such as water and methylene iodide, on the stickie surface\textsuperscript{36}. The contact angles and the surface energies of the liquids are then substituted into the Young equation to find the unknown surface energy of the stickie surface\textsuperscript{36}. While surface energy is related to tack it cannot be directly measured and does not necessarily predict the stickiness of a surface. Tack can be directly measured and is the metric of interest; thus tack will be used as the standard test for determining detackification. The tack can be determined using a device that measures how much force is required to remove a probe from the surface\textsuperscript{32,33}. The polar contribution to surface energy is determined by measuring the contact angle of water drop on the stickie surface, which is also used as a
direct measurement of hydrophobicity\textsuperscript{36,69}. Water drop contact angle will be used as the standard test for hydrophobicity.

Evidence suggests that it is possible to oxidize and subsequently raise the surface energy and decrease the hydrophobic nature of polymers using a wide variety of processes in gaseous environments\textsuperscript{49,50,51,52,53,54}. There is some also some evidence of oxidization of polymeric stickies in recycled pulp. Naddeo\textsuperscript{80} et al. has studied the use of oxygen based bleaching methods for recycled pulp. They found that polycrylate and styrene butadiene rubber (SBR), both pressure sensitive adhesives, were almost completely detackified using a proprietary oxygen bleaching sequence. The authors did not give a rationale for why the stickies were detackified, but a probable mechanism was that oxygen bleaching oxidized the surface of the stickie. The only other research done in this area was by Markham\textsuperscript{81} et al. who also studied oxygen bleaching of secondary fiber. They found that during oxygen bleaching of recycled fiber, stickies were not removed from the pulp. Nonetheless, they did not consider the tack, which was clearly a missed opportunity.

Sonochemical cavitation is a promising but underutilized method for creating free radicals, mainly hydroxyl, in water\textsuperscript{35}. Cavitation produced from an underwater discharge or ultrasound could be used to create hydroxyl radicals in order to oxidize stickie surfaces\textsuperscript{35,57,67,70}. It has been documented that cavitation produced hydroxyl radicals combine with polymer surfaces. Cavitation will occur as long as the shock wave pressure is greater than atmospheric pressure (1 atm) minus the vapor pressure of the water (\textapprox0.09 atm at 45°C)\textsuperscript{82}. Entrained air on the stickie surface could provide potential nucleation sites for cavitation and the resultant free radical reactions or stickies that are in the region of the cavitation collapse could also react with the resultant free radicals.
An underwater discharge using high voltage and current, called electrohydraulic discharge (EHD), is a well-documented source of cavitation. The pressure of the EHD compression wave has been shown to be from 5 to 270 atm. EHD equipment is relatively inexpensive. Additional information must be gathered about hydroxyl radical formation rates of an EHD device; however, this could be easily determined with a oxidation rate study. Also, Page has shown that after 100 discharges there is no observable effect on fiber properties, which is positive for treating stickies in pulp slurries.

Ultrasonic cavitation is commonly utilized for most laboratory sonochemical studies. However, capital and operating costs tend to be prohibitive on an industrial scale. The mechanism of hydroxyl radical formation for both EHD and ultrasound are known to be sonochemical cavitation. Accordingly, EHD will be used to test for sonochemical detackification of stickies. Ultrasonic treatment of stickies will serve as an independent mechanism confirmation.

Many phenomena are associated with an electrohydraulic discharge, including uv radiation, a plasma channel, a high pressure shock wave, and resultant cavitation, all of which have the potential to oxidize stickie surfaces. About 36% of the energy of the discharge is converted to uv radiation. High-pressure shock waves can apply high associated shear on surfaces, which could degrade the polymer surface. This degradation would only remove a layer of the surface, but the remaining bulk layers would still be tacky. Additionally, Mason found that polymers, such as PVAc were degraded by sonochemical cavitation, not by shock wave shear.

The most likely source of EHD generated hydroxyl radicals is from sonochemical cavitation, which is the result of the high-pressure acoustical shock wave, which
originates from the plasma channel\textsuperscript{72}. It would be interesting to determine whether or not radicals from sonochemical cavitation can modify stickie surfaces. The hydroxyl radicals, which have been shown to bond to polymer surfaces\textsuperscript{64}, should oxidize the stickie surface in order to decrease the hydrophobicity and increase the surface energy, which reduces tack. Another potential modification could be the crosslinking of the stickie surface\textsuperscript{49}, which could result in increased screenability due to the hardening of the stickie surface. Crosslinking in the case of polyacrylate or PVAc is the result of the breaking of C-H or C-C bonds and subsequent formation of carbon bonding to other polymer chains\textsuperscript{55,57,64}.

2.4 Hypothesis

Based on the literature, the most problematic stickies, polyacrylates and PVAc, can be detackified by increasing surface energy and decreasing hydrophobicity. One way to increase surface energy is to add polar functionality to the surface of the stickies\textsuperscript{36,49}, which can be accomplished by bonding oxygen to the polymer surface\textsuperscript{59}. This additional oxygen on the surface will also decrease the hydrophobicity\textsuperscript{46,49}. Additionally, both tack and hydrophobicity can be directly measured. EHD is a source of sonochemical cavitation, which can produce free radicals, mainly hydroxyl, that are available to oxidize stickie surfaces\textsuperscript{71}. Therefore, the following hypothesis is proposed:

The tack and hydrophobicity of stickies are decreased through surface oxidation by free radicals generated by EHD induced sonochemical cavitation.

2.5 Objectives

The objectives have been divided into two groups: the first investigate the fundamentals of EHD detackification and the second applications based experiments.
culminate in a mill trial. In order to understand the mechanism of stickie detackification by an electrohydraulic discharge, it is necessary to fulfill the following objectives:

1. Determine the main mechanism of detackification.
2. Establish the oxidation rates of EHD.
3. Quantify the effect of discharge voltage and intensity on free radical generation and detackification.

After determining the most probable mechanism of detackification, the second set of objectives examines EHD under different recycled paper mill conditions. The following applications based objectives are evaluated to perform a mill trial:

4. Investigate the effect of temperature, pH, fiber consistency, chemical additives, and distance on EHD detackification.
5. Examine the increased screenability of EHD treated problematic stickies.
6. Demonstrate the technical feasibility of EHD stickie detackification on an industrial scale.

2.6 Experimental Approach

The experimental approach provides an overview of the experiments that will test the hypothesis as well as support the reasoning behind chosen materials and testing procedures. The approach concludes with a mill trial. A more detailed description of the experimental procedures is in Chapter 3. The following subsections are divided into three parts. The first justifies the chosen materials and testing procedures that are common to many of the experiments. The second includes objectives that fundamentally describe the mechanism of EHD detackification. The third addresses objectives that
determine the best operating conditions and potential process locations under which EHD
detackification can occur in order to plan and carry out a mill trial.

2.6.1 Materials and Methods

It has been established that the most problematic stickies are polyacrylate and
PVAc, thus they will be used to test for EHD surface modification. The model stickies
selected are a brand of polyacrylate that is used in the adhesives industry and brand of
PVAc that is used as a commercial binder. Most of the experiments test the effects of a
wide variety of variables on polyacrylate detackification, with a few focusing on PVAc
surface modification.

Tack and hydrophobicity are directly measured in order to determine the extent of
EHD surface modification. Standardized tack and hydrophobicity tests require a smooth
surface, which round stickies or particles could not provide. Thus for most of the
studies, polyacrylate films are used. The stickie films serve as a model for actual mill
stickies. Both model stickies selected are used commercially and could be found in paper
products. Tack is dependent on film thickness when the film is 0.25mm thick; thus the
polyacrylate films are thicker than 0.25mm. The stickie films are formed on rigid
stainless steel backing in order to provide a constant shape in water and allow for Instron
tack testing. Stickies on paper or board backing might be subjected to tension as the
fibers when wet and compressive forces during drying. Also, paper or board might tear
or provide some energy dissipation during tack testing. There is no standard tack test for
PVAc since it is not tacky at room temperature, but hydrophobicity is measured.

Detackification is measured by tack and hydrophobicity is measured using water
drop contact angle. Tack is defined as the force required to remove a probe from a stickie
surface. The reduction of force needed to remove a probe from the surface relates to
the increase in detackification. The Instron tensile tester is an apparatus used to measure fracture force, which is similar to separation. Water drop contact angle is commonly used as a measure of hydrophobicity. A small amount of water is released onto the surface and the contact angle is measured by taking a picture of the droplet and using a computer program to determine the water contact angle with respect to the stickie surface. A decrease in water contact angle relates to a decrease in hydrophobicity.

2.6.2 Mechanism

The main purpose of the experimental approach is to test the hypothesis that EHD can detackify and decrease hydrophobicity of problematic stickie surfaces through free radical oxidation. The proposed mechanism is that EHD induced oxidation of polymer surfaces will decrease hydrophobicity and increase surface energy, thereby reducing tack. The first objective is to determine the main mechanism of detackification. The second objective is to establish the oxidation rates of EHD. The third objective is to quantify the effect of discharge intensity on free radical generation and detackification.

Before the mechanism is investigated, it must be established that stickie surfaces are actually detackified and that hydrophobicity is decreased by EHD treatment. This is accomplished by exposing polyacrylate films on rigid backing to a number of discharges in water, then measuring the tack, which is the force required to separate a probe from the stickie surface, and measuring hydrophobicity, which is the water drop contact angle. These results are then compared to controls that are placed in water for the same amount of time, without EHD treatment. Enough measurements are taken to ensure statistical significance. Once the detackification of stickies using EHD is established, then the mechanism is examined.

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The next step is to determine the fundamental mechanism of EHD detackification. There are three potential mechanisms: oxidation due to UV radiation, oxidation due to cavitation, and shock wave pressure\textsuperscript{[38,39].} UV oxidation is commonly determined by measuring the conversion of Fe\textsuperscript{2+} to Fe\textsuperscript{3+} at 350 nm, which is the wavelength of Fe\textsuperscript{3+} absorbance\textsuperscript{[35].} This is tested using a solution of ferrous sulfate as the source of Fe\textsuperscript{2+}; in water that will be exposed directly to EHD and sealed in quartz test tubes, which can transmit UV radiation\textsuperscript{[49].} If UV is an oxidative source, then samples from the quartz test tubes should show an increase in Fe\textsuperscript{3+} content. If they do not, then UV can be ruled out. Next, the effect of the high pressure shock wave is determined using two methods. The first is with a polyacrylate film on a rigid backing turned away from the EHD source, about 1 cm from the side of the tack. This prevents direct contact with the shock wave, but allows for transfer of free radicals formed in the water near the film. The tack and hydrophobicity are then compared with coupons with polyacrylate films that faced the shock wave. The second subjects a polyacrylate film on a rigid backing to a mechanically generated high pressure force. The tack and hydrophobicity is then compared before and after being subjected to high pressure. If there are no changes, then the effect of the pressure can be ruled out.

In order to determine oxidation of the stickie, the surface must be analyzed. X-ray photoelectron spectroscopy (XPS) is useful in determining the oxidation of polymer surfaces from 2 nm to 10 nm\textsuperscript{[48,49].} Also, FTIR analysis is performed in order to see if the bulk, up to 5 µm, has been oxidized. Polyacrylate and PVAc films are subjected to EHD treatment under a variety of conditions and then examined using XPS, which can measure oxygen to carbon ratios, and compare the levels to the levels of untreated controls. An increase in the oxygen to carbon ratio provides support for oxidation as a
key mechanism. An independent test for oxidation is surface pH. Polyacrylate films that are subjected to EHD treatment are analyzed for surface pH. The surface pH decreases if there are acidic groups added to the polymer surface, thereby documenting more evidence to support oxidation. Additional evidence for free radical oxidation will be established by subjecting polyacrylate coupons to EHD in the presence of sodium hypochlorite. The polyacrylate could have more significant tack decreases compared to samples exposed to EHD only in water, since sodium hypochlorite can provide chlorite ions, which can be radicalized by free radicals. Also, chlorine may be bonded to the surface, which can be detected by XPS. After establishing that stickie surfaces are indeed oxidized by EHD, it becomes evident that the source of oxidation must be determined.

The final step for the first objective is to provide evidence that free radicals are available for stickie surface oxidation. Therefore, it must be established that free radicals are produced by EHD. This supports the hypothesis by verifying that free radicals are the main source of oxidation agents from EHD. One way to do this is to measure the oxidation of ferrous sulfate solution in the presence of various concentrations of sodium acetate, whose known oxidation rate with hydroxyl radicals is used as a reference.

The second objective determines the changes in polyacrylate tack and hydrophobicity for independent exposure to EHD and ultrasound. Ultrasonic detackification can provide additional support for the hypothesis because ultrasound produces free radicals through cavitation without producing uv.

The third objective is to determine the effect of the voltage and intensity from EHD. This is done by establishing the effect of discharge voltage on free radical generation and detackification. The effect of voltage on free radical generation is measured by the oxidation potential of ferrous sulfate solutions. The tack of polyacrylate
films is also measured as a function of voltage. Similarly, the intensity is increased by increasing the number of discharges. The effect of the number of discharges on free radical generation is quantified using the oxidation potential of ferrous sulfate solutions and tack. Additionally, by comparing oxidation potential measurements with tack, the minimum intensity necessary for detackification is established.

The first part of the experimental approach provides evidence that the mechanism of detackification of sticky surfaces is most likely free radical oxidation, and it establishes the minimum intensity requirements for EHD induced detackification. EHD detackification can then be optimized in mill conditions. A mill trial is then performed to determine the real world detackification potential of EHD.

2.6.3 Application

Following the establishment of the fundamental mechanism, the subsequent objectives are investigated in order to apply the EHD detackification process in a mill setting. In order to accomplish this, the effects of several process parameters must be known in order to understand under which conditions is EHD most effective in the recycle paper manufacture process.

The fourth objective is to understand the effect of several key parameters on EHD detackification in order to assess its technical feasibility in a recycled paper mill. The parameters are temperature, pH, fiber consistency, chemical additives, and distance. The parameters are varied based on potential mill conditions in order to test for detackification over a wide variety of operating environments. Temperature, pH, and fiber consistency changes are straightforward. For example, the temperature is varied from 15°C to 45°C and pH is varied from 5 to 10, which is the range of most recycle mills. Fiber consistency is varied based on thin stocks of 0.5% and 1.0% and thick
stock of 3.5% [8]. The effect of EHD on the tack of polyacrylate in the presence of two common recycle paper mill additives is also examined. The two commonly used chemical additives in recycle paper mills are the detackifying agent DADMAC and a cationic retention aid. The effective range of the EHD is also determined through a distance study. Distance is varied using tanks up to 4.5 m long. Both tack and water contact angle of polyacrylate films are quantified as measures of detackification and hydrophobicity.

The fifth objective is to examine the possibility that exposure to EHD make the stickie less deformable. Less deformable stickies in the size range of screens are more likely to be rejected. This is tested by discharging stickies in suspension and then using a fine pressure screen to determine rejection rates, which is compared to controls of the same size range.

Finally, the sixth objective is to test the EHD device in a recycle mill that has problematic stickie build-up on machine surfaces, such as dryer cans and felts. The EHD unit is placed in the stuff box, which has pulp flow approaching the headbox. The ultimate goal is to reduce the downtime, which is quantified and compared to previous months without EHD treatment. This also increases production, extends the life of the felts, and saves on chemical costs.
CHAPTER 3. EXPERIMENTAL

Section 2.6, the Experimental Approach, gives the reasoning behind material and test method selection. Chapter 3 provides descriptions of the electrohydraulic discharge (EHD) apparatus, two of the discharging tanks, the materials, and the testing methods used, as well as the specific testing procedures for all of the experiments.

3.1 Electrohydraulic Discharge Apparatus

The main components of an EHD device are a constant current power supply (50,000 amps), high voltage oil filled capacitors (6,500V), a high current/high voltage switch, embedded controller, and a submersible discharge assembly with feeding electrode system. A commercially available EHD unit from Sparktec Environmental, Canada, is shown in Figure 22. When the EHD unit is turned on the capacitors are rapidly charged with electricity. At a pre-set voltage, the high voltage/high energy switch releases the stored energy from the capacitors to either the submersible electrode assembly or a set of integrated electrodes in a small section of pipe. The electric energy bridges the gap at the electrodes causing an arc that generates the plasma, which generates a shock wave and UV radiation. The gap length is typically 4.2m, which is preset on the Sparktec device.

Experiments using the submersible electrode assembly were conducted in a 130L concrete tank shown in Figure 23. The other assembly used was a 10L tank constructed from a section of pipe with integrated electrodes as shown in Figure 24.
Figure 22. The submersible EHD electrode assembly (white) with power supplies (black).

Figure 23. Illustration of the EHD submersible unit immersed in a 130L concrete tank.
3.2 Materials and Testing Methods

Section 3.2 describes the materials used for the majority of the experiments and the testing methods that are common to more than one experiment. Most of the mechanistic and applications studies require the measurement of tack and hydrophobicity of polyacrylate films on metal coupons subjected to various EHD treatments. Thus the stickie film selection and preparation are described in the next section, as well as the procedures for tack and hydrophobicity testing. Materials and testing methods that are specific to one experiment are explained in the description of that study.

3.2.1 Polyacrylate and PVAc Films

Carbotac® 26171 acrylic emulsion from BF Goodrich (Cleveland, OH) was used as the representative polyacrylate. Vinac® 884 vinyl acetate emulsion from Air Products (Allentown, PA) was used as the representative polyvinyl acetate (PVAc). 316L stainless steel coupons measuring 25cm² were used as substrats for both the polyacrylate and PVAc for the majority of the experiments. Each coupon had a unique number etched on the backside in order to identify samples.
Polyacrylate and PVAc films were made by placing a coupon in a polyacrylate or PVAc emulsion for five seconds, then removing and drying for one hour at 25°C. This was repeated two times until the film thickness was about 0.5mm. The film thickness was measured using a water drop analyzer stage and a viewer that had 5X magnification. A ruler that has 0.1mm divisions was used. The baseline was set at the interface between the metal coupon and the polyacrylate film. The measurements were recorded as the length of the film in the vertical direction and had the units of mm. The samples were then placed in petri dishes and sealed until experimental treatment. A polyacrylate coupon is shown in Figure 25. All references hereafter to polyacrylate films and coupons signify Carbotac® 26171 polyacrylate on 316L stainless steel coupons, unless otherwise noted. All references to PVAc films hereafter signify Vinac® 884 PVAc on 316L stainless steel coupons.

Figure 25. Polyacrylate film on stainless steel coupon.
3.2.2 Tack Testing

Polyacrylate tack was measured using the American Standards and Testing Methods (ASTM) tack test procedure for pressure sensitive adhesives (PSA). Tack was measured as the force required to separate the tip of a flat stainless steel probe from the polyacrylate surface. The test method was performed according to the ASTM standard test D2979-95, using an Instron tensile tester, from Instron (Canton, MA), as the force measuring apparatus. The 304 stainless steel probe had a surface area of 4.5 cm². The probe tip was cleaned with a small amount of acetone after each tack measurement. The initial contact pressure is 100 g/cm² with a one second dwell time and a 1 cm/second testing rate. The tack force was measured as g/cm², which is the standard for PSAs. Three tack measurements were taken for each polyacrylate sample and the average was reported.

3.2.3 Hydrophobicity Testing

The hydrophobicity was determined by measuring a water drop contact angle on the polyacrylate or PVAc surface. The test method was performed according to ASTM standard test method D5946-99, the standard test method for corona-treated polymer films using water contact angle measurements. The water drop volume was 5 μL. A digital picture of the water drop on the surface was taken, and the contact angle in degrees was determined using the FTA200 computer program from First Ten Angstroms (Portsmouth, VA). The FTA computer program takes a still photograph of the water drop on the surface. Then a baseline is drawn on the screen at the interface between the water drop and the sticky surface. Three points are then drawn on the water drop curve. The FTA computer program then gives a best-fit curve, connecting the three points on the curve.
water drop, and also gives a contact angle measurement of the water drop on the stickie surface. Three contact angles were taken for each sample and the average was reported.

3.2.4 Oxidation Potential

The oxidation potential and the ability of EHD to produce free radicals were both determined by measuring the conversion of Fe^{2+} to Fe^{3+}. One mM of ferrous sulfate solution, from JT Baker (Phillipsburg, NJ), was used as the source of Fe^{2+}. The amount of Fe^{3+} generated by EHD treatment was determined from the uv absorbance using a uv spectrophotometer of the solutions at 350nm. A curve for Fe^{3+} molar concentration versus absorbance at 350nm was established in order to convert absorbance values into concentrations since the rise of absorbance with increasing concentrations is linear. Because some Fe^{3+} was always present in the unreacted ferrous sulfate solution, the molar concentration was reported as \( \text{Fe}^{3+}_{\text{final}} - \text{Fe}^{3+}_{\text{initial}} \).

3.3 Mechanistic Studies

Section 3.3 details the experiments that test the following hypothesis: EHD can detackify and decrease the hydrophobicity of problematic stickie surfaces through free radical oxidation. Additionally, EHD oxidation rate studies are performed to compare with ultrasound. The section ends by establishing the discharge voltages, intensities, and distances required for EHD detackification.

3.3.1 Detackification Mechanism

The first experiments establish EHD as a means of detackifying stickies. The mechanism was then investigated by ruling out uv and shock wave pressure as oxidation and detackifyng mechanisms. Studies were performed to support EHD oxidation of the stickie surface, such as XPS analysis, and surface pH. The final experiments were
discharging in the presence of hypochlorite and peroxide and a hydroxyl rate study, in order to provide support for a free radical mechanism.

3.3.1.1 EHD Detackification and Decrease in Hydrophobicity

The first experiment was performed to establish that stickie surfaces were detackified and that hydrophobicity was decreased by EHD treatment. Polyacrylate coupons were subjected to 30 and 60 discharges in the small 10L tank. Polyacrylate tack and hydrophobicity was measured three times for each experimental set, and the average for each was reported. The results of the discharged samples were then compared to tack and hydrophobicity values of controls that were placed in water for the same amount of time, but were not discharged. PVAc coupons were also subjected to 1 and 10 discharges in the 10L tank at 6,500 volts. The hydrophobicity was measured three times for each of the treatments and the averages were reported. The PVAc results were then compared to the hydrophobicity values of a control coupon that was placed in water for the same amount of time, but was not discharged. Also, polyacrylate on linerboard backing was discharged 30 times at 6,500 volts in the 10L tank in order to determine if EHD could reduce the hydrophobicity of stickies not on metal substrates. The hydrophobicity was measured for the treated polyacrylate, and a polyacrylate control that was also on a linerboard backing and placed in water for the same amount of time, but not subjected to discharge.

3.3.1.2 UV and Shock Wave Pressure

The next set of experiments was performed to rule out uv and shock wave pressure as oxidation and detackifying mechanisms, respectively. For the first experiment, the 10L tank was filled with a 0.175 M solution of ferrous sulfate and was exposed directly to 20, 40, and 60 discharges at 6,500 volts, with 10mL removed after
each treatment for analysis. Next, a 0.175 M solution of ferrous sulfate was contained in 10mL quartz test tubes, which were then submerged in the 10mL tank filled with tap water and subjected to 20 and 40 discharges. The amount of Fe$^{3+}$ generated by EHD treatment for each treatment was determined from the uv absorbance of the solutions at 350nm. The change in Fe$^{3+}$ concentration was then compared for both treatment sets.

The next two experimental sets were done to rule out the high pressure shock wave as the detackifying mechanism. Polyacrylate coupons were placed in the 130L tank both facing and turned away from the electrode discharge source. The samples were about 1cm from the back wall, with both samples about 50cm from the discharge source. Tack and hydrophobicity were measured three times for both treatment sets and reported as an average, which were compared to a control sample that was placed in water for the same amount of time, but not subjected to discharge. The second set tested the tack and hydrophobicity of polyacrylate coupons before and after being subjected to a direct pressure force of 100 atm for thirty repetitions. The source of the pressure was the IPST MTS press, which is a platen press used to simulate impulse drying. A silicon release paper was placed between the polyacrylate surface and the platen in order to avoid sticking.

3.3.1.3 Oxidation of Stickie Surfaces

The following experimental sets were performed to provide evidence of stickie surface oxidation. Polyacrylate and PVAc coupons were subjected to 40 discharges in tap water at 6,500 volts in the 10L tank. Additionally, a polyacrylate coupon was discharged 40 times at 6,500 volts in tap water with 500 ppm of sodium hypochlorite added. The changes in surface chemistry that accompany tack reduction were measured by X-ray photoelectron spectroscopy (XPS) at the Georgia Tech Research Institute.

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Quantitative results from the XPS studies were reported as the O:C ratio and compared to the O:C ratio of polyacrylate and PVAc controls that were not subjected to discharges. FTIR analysis was also performed at the Institute of Paper Science and Technology on polyacrylate coupons discharged 40, 500, and 1000 times in tap water, which were compared to an untreated control.

The pH of polyacrylate coupons that were discharged 40, 500, and 1000 times at 6,500 volts in the 10L tank was measured by placing a 1mL drop of de-ionized water onto the stickies surface. Then pH indicator strips were placed on the water drop for one minute and the pH was recorded.

3.3.1.4 Free Radical Oxidation

In order to support a free radical detackification mechanism, polyacrylate coupons were exposed to EHD 30 times in tap water with 500 ppm of sodium hypochlorite at 6,500 volts in the 10L tank. Tack and hydrophobicity were measured three times for both treatment sets and reported as an average, which were compared to a control sample that was placed in water with 500 ppm of sodium hypochlorite for the same amount of time, but not subjected to discharge. The polyacrylate coupons discharged in sodium hypochlorite were also compared with the tack and hydrophobicity of polyacrylate coupons that were subjected to 30 discharges in tap water.

In order to establish that hydroxyl radicals were generated from EHD, the oxidation of 1.0 mM of ferrous sulfate, a source of Fe^{2+}, was monitored in the presence of 0.5, 1.0, and 2.0 mM of sodium acetate. Each mixture was subjected to 100 discharges at 5,000 volts in the 10L tank. The amount of Fe^{3+} generated by EHD was determined from the UV absorbance of the solutions at 350nm. The rate constant for the reaction of Fe^{3+}, k₂, was determined from a rate equation that was developed from the competitive reaction
of Fe$^{2+}$ with hydroxyl radical in the presence of sodium acetate and the reaction of Fe$^{2+}$ with hydroxyl radical alone. The ferrous sulfate oxidation reactions can be represented by the reaction of Fe$^{2+}$ with the hydroxyl radical, OH$^-$, as shown below:

$$\text{Fe}^{2+} + \text{OH}^- \rightarrow \text{Fe}^{3+} + \text{OH}^-$$

The ferrous sulfate and sodium acetate reactions can be represented by the two competitive reactions of Fe$^{2+}$ and Na$^+$ with the hydroxyl radical, OH$^-$, shown below:

$$\text{Fe}^{2+} + \text{OH}^- \rightarrow \text{Fe}^{3+} + \text{OH}^-$$
$$\text{Na}^+ + \text{OH}^- \rightarrow \text{Na}^{2+} + \text{OH}^-$$

When there is no sodium acetate in the system the concentration of reacted Fe$^{2+}$ is given by $A_0$ in the following rate equation:

$$\frac{d[\text{Fe}^{2+}]}{dt} = A_0 = k_2[\text{Fe}^{2+}][\text{OH}^-]$$

When sodium acetate is present in the system the concentration of reacted Fe$^{2+}$ is given by $A$ as follows:

$$\frac{d[\text{Fe}^{2+}]}{dt} = A = k_2[\text{Fe}^{2+}][\text{OH}^-]'$$

$[\text{OH}^-]'$ is the concentration of hydroxyl radical that reacts with Fe$^{3+}$, and $[\text{OH}^-]$ represents the total concentration of both Fe$^{2+}$ and Na$^{2+}$ that has reacted. The ratio of $[\text{OH}^-]'$ to $[\text{OH}^-]$ is the ratio of the amount of Fe$^{2+}$ reacted to the sum of the amounts of Fe$^{2+}$ and Na$^{2+}$ reacted as follows:

$$\frac{[\text{OH}^-]'}{[\text{OH}^-]} = \frac{k_2[\text{Fe}^{2+}]}{k_2[\text{Fe}^{2+}]+k_1[\text{Na}^+]}$$

Therefore, $[\text{OH}^-]'$ can be written as:

$$[\text{OH}^-]' = \frac{k_2[\text{Fe}^{2+}][\text{OH}^-]}{k_2[\text{Fe}^{2+}]+k_1[\text{Na}^+]}$$

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A rate equation based on the reactions of Fe$^{2+}$ with and without sodium acetate can be developed by dividing $A$ by $A_0$. This rate equation can then be used to solve for the rate constant, $k_3$, in order to compare to known values from the literature. Literature values for $k_1$ will be used to solve the equation for $k_2$. Hydroxyl radical oxidation can be supported if the values for $k_2$ that were determined experimentally and from the literature are close. To solve, given the experimental data, $A_0/A$ is plotted against the proportions of the initial concentrations of sodium acetate to ferrous sulfate. The equation of the line is determined and the slope represents $k_1/k_2$. Then $k_3$ is found by using the slope of the line and the literature value of $k_1$. The final rate equation for $A_0/A$ follows:

$$\frac{A_0}{A} = 1 + \frac{k_1}{k_3} \left[ \text{sodium acetate} \right] \left[ \text{ferrous sulfate} \right]$$

3.3.2 Ultrasound Detackification

In order to determine the detackification and hydrophobicity effects of ultrasound treatment, polyacrylate coupons were subjected to 10, 20, and 40 minutes of ultrasonic treatment in a one liter ultrasonic bath with a frequency of 20kHz and an intensity of 30W/cm$^2$. The ultrasonically treated samples were tested for tack and water drop contact angle$^9$. EHD tack and hydrophobicity results were also measured for 20, 40, and 60 exposures to EHD as a reference, but not as a direct comparison, due to the time and intensity differences between ultrasound and EHD.

3.3.3 Discharge Voltage and Intensity

In order to determine how the applied voltage affected the generation of free radicals, 1.0 mM of ferrous sulfate was subjected to discharges at 2,000 and 6,500 volts in the 10L tank. The oxidation potential of ferrous sulfate subjected to both voltages was determined following the procedure provided in section 3.2.4. The change in Fe$^{3+}$
concentration was also compared with a number of discharges, which revealed the effect of discharge intensity on free radical formation. In addition, polyacrylate coupons were subjected to 10, 30, and 60 discharges at 6,500 volts in the 10L tank. Polyacrylate tack and hydrophobicity were measured three times for each experimental set, and the average for each was reported.

3.4 Applications Studies

Section 3.4 explains the applications-based experiments. The first set of experiments examines the effect of process parameters on EHD detackification. Next, the effect of EHD on screenability of stickies in suspension is analyzed. Finally, an EHD mill trial in a 100% recycled linerboard mill is performed.

3.4.1 Process Parameters

The effects of several process parameters on EHD detackification and hydrophobicity were determined in order to assess its technical feasibility in a mill environment. The parameters investigated in laboratory studies were: temperature, pH, fiber consistency, chemical additives, and distance.

3.4.1.1 Temperature

Polyacrylate coupons were subjected to 30 and 60 discharges in the 10L tank with water at temperatures of 15°C, 22°C, and 45°C. Polyacrylate tack and hydrophobicity were measured three times for each experimental set, and the average for each was reported. The results of the discharged samples were then compared to tack and hydrophobicity values of controls that were placed in water for the same amount of time, but were not subject to discharge.
3.4.1.2 pH

Polyacrylate coupons were subjected to 40 discharges in the 10L tank with water at pHs adjusted to 5, 7, 9, and 10. The pH was made acidic (pH 5) by adding amounts of sulfuric acid, and the pH was made more basic (pH 9 and 10) by adding sodium hydroxide. Polyacrylate tack and hydrophobicity were measured three times for each experimental set, and the average for each was reported. The results of the discharged samples were then compared to tack and hydrophobicity values of controls that were placed in the same pH adjusted water for the same amount of time, but were not discharged.

3.4.1.3 Fiber Consistency

Polyacrylate coupons were subjected to 40 discharges in the small 10L tank in the presence of 0.5%, 1.0%, and 3.5% consistency bleached kraft softwood pulp suspensions. Polyacrylate tack and hydrophobicity were measured three times for each experimental set, and the average for each was reported. The results of the discharged samples were then compared to tack and hydrophobicity values of controls that were placed in the 3.5% consistency pulp suspension for the same treatment time, but were not discharged.

3.4.1.4 Chemical Additives

Polyacrylate coupons were subjected to 40 discharges in the small 10L tank in the presence 0.1% by weight cationic retention aid from Nalco, and 0.1% by weight Twern surfactant from ICI International (Wilmington, DE), in two separate experiments. Polyacrylate hydrophobicity was measured three times for each experimental set, and the average for each was reported. The results of the discharged samples were then compared to hydrophobicity values of controls that were placed in the same chemical additive over the same treatment time, but were not discharged.
Polyacrylate coupons were subjected to 10 discharges in the 10L tank in the presence 0.1% by weight DADMAC from 3V (Weehawken, NJ). Polyacrylate tack was measured three times for the experimental set, and the average was reported. The result of the discharged samples was then compared to tack value of the control that was placed in the same chemical additive for the same treatment time, but was not discharged.

3.4.1.5 Distance Studies

Water (4,000L) containing 1.9 mM of ferrous sulfate was sparked in a 1m deep tank with the submersible sparker placed flush against the wall at one end to determine the oxidative range of EHD. The 4,000L tank is shown in Figure 26. Samples were collected after 1, 20, 40, 60, and 100 sparks at distances of 10cm, 1.5m, 3m, and 4.5m away from the source at a depth of 10cm from the surface. Their UV absorbances at 350nm were taken immediately after each discharge set in order to determine the concentration of Fe$^{3+}$ created upon EHD treatment at different distances away from the discharge.

![Figure 26. Illustration of the 4,000L tank used for distance studies.](image)

Additionally, polyacrylate coupons were placed 10cm, 50cm, and 1.5m from the EHD source at a depth of 10cm from the surface, because the EHD electrode gap was
submerged 10 cm from the surface. The tack was measured three times for EHD treated polycrylate samples and reported as the average. The tack of the treated samples was then compared to the tack of a polycrylate control that was place in water for the same treatment time, but was not discharged.

3.4.2 Stickie Screenability

A stickie emulsion, Carbotae®, was dried on a glass plate and mechanically homogenized in water with one mM of sodium silicate surfactant. The surfactant allows the stickie to be suspended in water. The stickie suspension was then diluted to 0.5% by weight in water. Ten liters of the 0.5% stickie suspension was subjected to 20, 40, and 60 discharges in the 10L tank, with 500ml removed after each set of discharges for analysis. The pressure screen rejection percentage was determined with a Pulmac® analyzer from Pulmac Instruments (Montpelier, VT) fitted with a 150μm screen. Rejection rates were repeated once for each treatment set and compared to the control, which was not subjected to discharge. The results were reported as percentage rejected.

3.4.3 Mill Trial

A full scale EHD trial was performed at the VISY Papermill in Conyers, Georgia. The mill produces on average 850 tons per day of 100% recycled two-ply linerboard. The dual headbox fourdrinier paper machine is shown in Figure 27. The furnish is 80% mixed office waste and 20% old corrugated containers, and contains various types of colloidal stickies. The EHD submersible electrode assembly was placed in the top liner stuff box, shown in Figure 28, which has a flow rate of about 6000L per minute and a pulp consistency of about 3.5%. The stuff box had a capacity of 1000L, meaning the average residence time was 10 seconds. The headbox pH is usually from 7.0-7.2. The
mill quantified the amount of time required to clean the Unirun® from Weavex dryer fabric, shown in Figure 29, in the first dryer section.

Figure 27. VISY linerboard machine.

Figure 28. Stuff box with submersible EHD unit.
Figure 29. VISY Unirun® dryer fabric.

The tack of the mill stickies before and after EHD treatment was also quantified by a colloidal stickie measurement developed and performed by Sung	extsuperscript{91}. Pulp samples from the top ply headbox were collected and filtered. Then 700mL of the filtrate was concentrated to 5mL at 100°C for four hours. The concentrate was then placed on a metal coupon and dried at 25°C for 12 hours forming a thin stickie film. The coupons were then immersed in water heated to 60°C for 10 seconds and the tack was then measured using a Polyken tack tester from Testing Machines Inc. (Islandia, NY). The tack was measured according to the same ASTM standard test method, D2979-95	extsuperscript{10} described in section 3.2.2 and was reported as grams/cm	extsuperscript{2}.
CHAPTER 4. MECHANISTIC RESULTS AND DISCUSSION

The first sets of experiments established that electrohydraulic discharge (EHD) detackified and reduced the hydrophobicity of stickies showing that EHD can be useful as a stickie control method. Then, the hypothesis that EHD oxidizes the stickie surface was tested. Ultraviolet (uv) radiation and shock wave pressure were both experimentally ruled out as detackifying mechanisms. X-ray photoelectron spectroscopy (XPS) studies revealed that surfaces treated with EHD had increased levels of oxygen. Also, stickie samples that were treated with EHD had lower pH. The increased oxygen on the surface and the decrease in pH support the hypothesized oxidation mechanism. It was also shown that EHD is a source of free radicals capable of oxidizing stickie surfaces. The final experiments determined that EHD treatment in the presence of sodium hypochlorite further decreased tack. Finally, the hydroxyl rate study provided further support for a free radical mechanism.

4.1 Mechanistic Studies

4.1.1 EHD Detackification and Decrease in Hydrophobicity

It was shown that EHD treatment of stickies reduced tack up to 50% and hydrophobicity by about 10%. Separately, polyacrylate films on metal coupons were subjected to EHD in both the 10L and 130L tanks and had decreases in both tack and hydrophobicity. These results are given Table 2. The standard deviation for the tack tests was 62.3g/cm² and for the hydrophobicity was 2 degrees. The tack and hydrophobicity statistics are given in Appendix I. A hydrophobicity measurement was also taken on a polyacrylate film on a linerboard backing that was exposed to EHD. A control sample of polyacrylate film on linerboard that was not subjected to EHD was also tested for hydrophobicity. The results of this test were very similar to the results of the
stickie film on metal coupons, indicating that decreasing the hydrophobicity did not require the stickies to have a hard base, but was also effective when the film was applied to a fibrous substrate.

**Table 2. Effect of EHD on polycrlylate tack and hydrophobicity.**

<table>
<thead>
<tr>
<th>Type of Stickie</th>
<th>No. of Discharges</th>
<th>Tack (g/cm²)</th>
<th>Hydrophobicity (degrees)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polycrlylate</td>
<td>0</td>
<td>1,350</td>
<td>91</td>
</tr>
<tr>
<td>Polycrlylate</td>
<td>30</td>
<td>640</td>
<td>78</td>
</tr>
<tr>
<td>Polycrlylate</td>
<td>60</td>
<td>690</td>
<td>78</td>
</tr>
<tr>
<td>Polycrlylate on linerboard</td>
<td>0</td>
<td>Not Tested</td>
<td>89</td>
</tr>
<tr>
<td>Polycrlylate on linerboard</td>
<td>30</td>
<td>Not Tested</td>
<td>73</td>
</tr>
</tbody>
</table>

Polyvinyl acetate (PVAc) coupons that were subjected to EHD in the 10L tank had a 15% decrease in hydrophobicity after being exposed to 10 discharges, but a single exposure to EHD had no measurable effect. The PVAc hydrophobicity results are given in Figure 30.

![Figure 30. Hydrophobicity of PVAc coupons before and after EHD treatment.](image)

**4.1.2 UV and Shock Wave Pressure**

Since the mechanism of detackification was believed to be chemical rather than physical in origin, a 0.175 mM FeSO₄ solution that responds to free radicals was exposed
to EHD in two ways in the small tank. The Fe$^{3+} \rightarrow$ Fe$^{3+}$ transition was monitored spectrophotometrically at 350nm. First, the 10L tank was filled with the solution and then exposed directly to EHD. The solution, contained in 10mL quartz test tubes that allow uv transmission, was submerged in the tank and then exposed to EHD. The results, illustrated in Figure 31 show that the solution in the quartz test tubes had no change in concentration, while the solution exposed directly to EHD changed concentration. These results indicate that it is the effect of the chemical species and not the uv that was responsible for the change in concentration.

![Effect of No. of Discharges on Ferrous Sulfate Oxidation in Direct Contact and UV Test Tubes](image)

**Figure 31. The contribution of uv to EHD oxidation.**

The next two experimental sets were performed to determine the role of the high pressure shock wave produced by the discharge as the deackifying mechanism. Polyacrylate films on metal coupons that were subjected to EHD facing and turned away from the electrode discharge source showed nearly identical decreases in tack and hydrophobicity. Also, polycrystalline coupons that were subjected 30 times to 100 atm direct force on the MTS press did not show any changes in tack or hydrophobicity, further ruling out shock wave pressure as a deackifying mechanism. The treated and
control polyacrylate tack and hydrophobicity results from these experiments are shown in Table 3.

<table>
<thead>
<tr>
<th>Type</th>
<th>Conditions</th>
<th>No. of Discharges</th>
<th>MTS Contacts</th>
<th>Tack (g/cm²)</th>
<th>Hydrophobicity (degrees)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyacrylate</td>
<td>Control</td>
<td>0</td>
<td>N/A</td>
<td>1.350</td>
<td>91</td>
</tr>
<tr>
<td>Polyacrylate</td>
<td>Toward (50cm)</td>
<td>30</td>
<td>N/A</td>
<td>640</td>
<td>81</td>
</tr>
<tr>
<td>Polyacrylate</td>
<td>Away (50cm)</td>
<td>30</td>
<td>N/A</td>
<td>863</td>
<td>76</td>
</tr>
<tr>
<td>Polyacrylate (MTS)</td>
<td>at 100 atm</td>
<td>N/A</td>
<td>30</td>
<td>1.362</td>
<td>90</td>
</tr>
</tbody>
</table>

4.1.3 Oxidation of Stickie Surfaces

In order to examine surface effects, the stickie films were subjected to EHD treatments and their surfaces examined by X-ray photoelectron spectroscopy (XPS). As shown in Table 4, the O:C ratio increased in all cases. Since the standard deviation for the XPS measurements was 0.01, the increases are significant. In contrast, FTIR analysis showed no changes in the bulk of the polyacrylate polymer, which means that EHD oxidation is probably limited to a 10nm depth on the stickie surface, the measurement limit of XPS.

<table>
<thead>
<tr>
<th>Stickie Type</th>
<th>Conditions</th>
<th>O:C ratio (± 0.01)</th>
</tr>
</thead>
<tbody>
<tr>
<td>polyacrylate</td>
<td>control, pH 7</td>
<td>0.28</td>
</tr>
<tr>
<td>polyacrylate</td>
<td>control, pH 7</td>
<td>0.28</td>
</tr>
<tr>
<td>polyacrylate</td>
<td>40 discharges, pH 7</td>
<td>0.32</td>
</tr>
<tr>
<td>polyacrylate</td>
<td>40 discharges, pH 7, 500 ppm sodium</td>
<td>0.30</td>
</tr>
<tr>
<td>polyvinyl acetate</td>
<td>Control</td>
<td>0.35</td>
</tr>
<tr>
<td>polyvinyl acetate</td>
<td>40 discharges, pH 10</td>
<td>0.42</td>
</tr>
</tbody>
</table>

Chlorine was detected by XPS at a level of 0.29% for the experiment run in the presence of sodium hypochlorite; there was no chlorine found for the other cases. These measurements strongly suggest a free radical mechanism, with detackification caused by...
oxidation of the surface. Sodium hypochlorite that is subjected to EHD should give rise to chlorine radicals, which are oxidative species that can attach to the surface of the stickie. The effect of sodium hypochlorite was further explored by subjecting a polyacrylate coupon in a 500 ppm sodium hypochlorite solution to EHD treatment. A control without sodium hypochlorite was also run. The results, shown in Table 5, confirm that detackification improves in the presence of hypochlorite, further supporting a chemical mechanism for the process. The tack decreased by about 80% and the hydrophobicity decreased about 15%.

Table 5. Tack of EHD treated polyacrylates in sodium hypochlorite solution.

<table>
<thead>
<tr>
<th>Type of Stickie</th>
<th>Conditions</th>
<th>No. of Discharges</th>
<th>Tack (g/cm²)</th>
<th>Hydrophobicity (degrees)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyacrylate</td>
<td>500 ppm sodium hypochlorite</td>
<td>0</td>
<td>840</td>
<td>87</td>
</tr>
<tr>
<td>Polyacrylate</td>
<td>500 ppm sodium hypochlorite</td>
<td>30</td>
<td>245</td>
<td>74</td>
</tr>
</tbody>
</table>

The pH of polyacrylate coupons that were EHD treated decreased with an increasing number of discharges. These results are shown in Figure 32. The pH results as well as the previously stated XPS results both suggest EHD induced oxidation of polymer surfaces.

![Figure 32. Polyacrylate pH changes due to EHD treatment.](image-url)
4.1.4 Free Radical Oxidation

In order to establish that hydroxyl radicals were generated from sparking, the oxidation of Fe\(^{2+}\) was monitored in the presence of various amounts of sodium acetate. Each mixture was subjected to EHD 100 times in a 10L tank, and the Fe\(^{2+} \rightarrow Fe^{3+}\) oxidation was monitored by spectrophotometry at 350nm. The results are provided in Figure 33. The rate of reaction of oxidation of Fe\(^{3+}\), \(k_2\), was found through competitive kinetics using sodium acetate as a reference from the following rate equation

\[
\frac{A_0}{A} = 1 + \frac{k_1}{k_2} \left[ \text{sodium acetate} \right] \left[ \text{ferrous sulfate} \right]
\]

where \(A_0\) and \(A\) are initial and instantaneous absorbances, and \(k_1\) (0.085 x 10\(^8\) L mol\(^{-1}\) s\(^{-1}\)) is the rate constant for sodium acetate oxidation by hydroxyl radical\(^{92}\). A rate constant of 4.9 \times 10\(^8\) L mol\(^{-1}\) s\(^{-1}\) obtained for \(k_2\) which compares well with the reported range of 3.2-4.3 \times 10\(^8\) L mol\(^{-1}\) s\(^{-1}\) for the oxidation of Fe\(^{2+}\) with hydroxyl radicals\(^{92}\). EHD induced hydroxyl radicals are available to react with stickie surfaces, giving further support to a free radical detackification mechanism.
Figure 33. Oxidation of ferrous sulfate and sodium acetate with hydroxyl radicals.

4.2 Ultrasonic Detackification

In order to determine the detackification effects of ultrasound, polycrylate coupons were subjected to 10, 20, and 40 minutes of ultrasonic treatment in a one liter ultrasonic bath with a frequency of 20kHz and intensity of 30W/cm² by Sung91. EHD results were also measured as a reference, but not a direct comparison, due to intensity and treatment time differences. The results given in Table 6 show that both EHD and ultrasonic treatment detackified stickie surfaces.

Table 6. EHD and ultrasonic detackification91.

<table>
<thead>
<tr>
<th>Type</th>
<th>No. of Discharges</th>
<th>Time Sonicated (min.)</th>
<th>Tack (g/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polycrylate</td>
<td>0</td>
<td>N/A</td>
<td>2,010</td>
</tr>
<tr>
<td>Polycrylate</td>
<td>20</td>
<td>N/A</td>
<td>1,998</td>
</tr>
<tr>
<td>Polycrylate</td>
<td>40</td>
<td>N/A</td>
<td>1,725</td>
</tr>
<tr>
<td>Polycrylate</td>
<td>60</td>
<td>N/A</td>
<td>1,419</td>
</tr>
<tr>
<td>Polycrylate</td>
<td>N/A</td>
<td>0</td>
<td>2,000</td>
</tr>
<tr>
<td>Polycrylate</td>
<td>N/A</td>
<td>10</td>
<td>1,689</td>
</tr>
<tr>
<td>Polycrylate</td>
<td>N/A</td>
<td>20</td>
<td>1,786</td>
</tr>
<tr>
<td>Polycrylate</td>
<td>N/A</td>
<td>40</td>
<td>1,284</td>
</tr>
</tbody>
</table>
4.3 Discharge Voltages and Intensity

In order to determine how the discharge voltage influenced the generation of free radicals, a solution of ferrous sulfate was subjected to EHD discharge at 2,000V and 6,500V. The results presented in Figure 34, show that the two conditions lead to increases in $\text{Fe}^{2+}$ oxidation with the 6,500V EHD generating more free radicals than the 2,000V treatment. However the 6,500V EHD condition does not create 3 times as many radicals.

![Graph showing change in ferrous sulfate concentration vs. number of discharges](image)

**Figure 34. Effect of voltage on radical generation.**

The effects of EHD intensity, defined by number of discharges at 2,000V and 6,500V, on ferrous sulfate oxidation and detackification were also determined. The change in $\text{Fe}^{2+}$ concentration compared to the number of discharges revealed that free radicals increased linearly with the number of discharges, regardless of voltage. These results are also shown in Figure 34.

Additionally, after 30 EHD exposures at 6,500V the polyacrylate tack was reduced compared to 10 exposures at 6,500V and the unexposed control. However, the
polyacrylate tack after 60 EHD exposures was nearly equal to the tack after 30 exposures. These tack results are given in Table 7.

Table 7. The effect of number of discharges on detackification.

<table>
<thead>
<tr>
<th>Type of Stickie</th>
<th>No. of Discharges</th>
<th>Tack (g/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyacrylate</td>
<td>0</td>
<td>1,350</td>
</tr>
<tr>
<td>Polyacrylate</td>
<td>10</td>
<td>823</td>
</tr>
<tr>
<td>Polyacrylate</td>
<td>30</td>
<td>640</td>
</tr>
<tr>
<td>Polyacrylate</td>
<td>60</td>
<td>690</td>
</tr>
</tbody>
</table>

4.4 Major Findings and Discussion

The major findings of the mechanistic studies were that exposure to EHD decreased the tack and reduced the hydrophobicity of polyacrylate stickies and reduced the hydrophobicity of PVAc. Based on this discovery a patent by the author of this dissertation and his advisor was filed, and is presented in Appendix II. Concurrent studies showed that the tack of pitch, wood resins, was also reduced after EHD treatment. Once detackification was established, the hypothesis that the tack and hydrophobicity of stickies are decreased through surface oxidation by free radicals generated by EHD induced sonochemical cavitation was tested. There was considerable evidence that EHD detackification was the result of free radical oxidation of the stickie surface. It was also found that stickie surfaces were chemically altered after exposure to EHD. XPS analysis of EHD treated stickies revealed direct evidence of surface oxidation. The pH of polyacrylate surfaces decreased after exposure to EHD, providing further evidence of an oxidation mechanism. EHD was also indirectly found from the ferrous sulfate and sodium acetate competitive rate study to generate free radicals, specifically hydroxyl radicals, which were the most likely source of oxidation. The incorporation of oxygen on the surface, and the decrease in pH and hydrophobicity build a strong case for the involvement of hydroxyl radicals in decreasing the tack of stickies.
Many phenomena are associated with an electrohydraulic discharge, including uv radiation, a plasma channel, a high pressure shock wave, and the resultant cavitation, all of which have the potential to modify stickie surfaces. It was first necessary to rule out uv oxidation and shock wave pressure as mechanisms of detackification. It was found that uv did not show any oxidation potential up to 40 discharges, probably because the water absorbed the uv radiation. The plasma channel can form free radicals and ozone, but the volume is only 3-4mL, which is localized around the electrode gap.

Polyacrylate stickies were detackified 50cm from the EHD electrodes, ruling out the plasma channel as the only source of free radicals. The high-pressure shock wave was also ruled out. Polyacrylate stickies that were subjected to 100atm of force were not detackified. The lack of surface modification due to the high pressure shock wave is consistent with Mason's finding that polymer surfaces are chemically altered by sonochemical cavitation, not mechanically by shock wave pressure.

In order to detackify stickies, EHD had to increase the stickie surface energy. This was done by increasing the polar contribution to surface energy by surface oxidation. Oxidation of polymer surfaces to raise the surface energy has been well documented. XPS results revealed that oxygen was bonded to polyacrylate and PVAc surfaces, increasing the polar contribution to surface energy. This is not surprising since hydroxyl radicals generated from sonochemical cavitation have been shown to bond to polymer surfaces. Additional support for an oxidation mechanism was that the pH decreased after EHD treatment.

Since it was shown that oxidation of the stickie surface did occur, the source of the oxidation was then examined. The most likely source of EHD generated free radicals is from sonochemical cavitation, which is the result of the high-pressure acoustic shock.
wave originating from the plasma channel\textsuperscript{67,71}. EHD was shown to generate free radicals linearly with number of discharges. It was shown through a rate study that hydroxyl radicals are formed. It was also found that ultrasonic treatment of stickie surfaces results in detackification\textsuperscript{91}. Ultrasonic detackification supports the hypothesis, in that ultrasound has no associated uv and sonochemical cavitation. The parallel between sonication and EHD suggests that both processes create hydroxyl radicals through cavitation, which then oxidize the polymer surface.

It was also found that there was EHD free radical generation at both 2,000V and 6,500V. This is of operational importance, since more discharges can be delivered per second at lower voltages, potentially increasing treatment volumes and extend electrode life. Furthermore, polyacrylate tack was reduced up to 50\% upon exposure to 30 electrohydraulic discharges; however, polyacrylate tack was not further reduced after 60 EHD exposures. This suggests that there is a limiting detackifying effect only in the presence of water, probably signifying that only so much of the stickie surface is oxidizable under EHD treatment conditions. However, further detackification of stickie surfaces is possible, since polyacrylates that were exposed to EHD in a solution of sodium hypochlorite were detackified up to 80\%.
CHAPTER 5. APPLICATIONS RESULTS AND DISCUSSION

The first set of applications based experiments examined the effects of process parameters on EHD detackification, finding that EHD detackifies stickies under a wide variety of process parameters. Next, screenability of stickies in suspension was shown to increase after 20 exposures to EHD. A mill trial in a 100% recycled linerboard mill was performed for five weeks, where the tack of mill stickies was found to decrease during exposure to EHD.

5.1 Process Parameters

The effects of several process parameters on EHD detackification and hydrophobicity on polyacrylate films were determined in order to assess its technical feasibility in a mill environment. The parameters investigated were temperature, pH, fiber consistency, chemical additives, and distance. EHD appears to detackify polyacrylates under many process conditions. The standard deviation for the tack tests was 62.3g/cm² and for the hydrophobicity was 2 degrees. The tack and hydrophobicity statistics are given in Appendix I.

5.1.1 Temperature

EHD was tested under three different temperatures with 30 discharges in order to determine its effectiveness at different points in the recycle process. The results show that tack was reduced by at least 50% at 15°C and 22°C. The results also show that tack was reduced by more than 60% at 45°C. These results are shown in Table 8.
Table 8. The effect of temperature on the tack and hydrophobicity of EHD treated polyacrylate films.

<table>
<thead>
<tr>
<th>Type</th>
<th>Temperature (°C)</th>
<th>No. of Discharges</th>
<th>Tack (g/cm²)</th>
<th>Hydrophobicity (degrees)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyacrylate</td>
<td>15</td>
<td>0</td>
<td>1.225</td>
<td>89</td>
</tr>
<tr>
<td>Polyacrylate</td>
<td>15</td>
<td>30</td>
<td>605</td>
<td>78</td>
</tr>
<tr>
<td>Polyacrylate</td>
<td>22</td>
<td>0</td>
<td>1.350</td>
<td>91</td>
</tr>
<tr>
<td>Polyacrylate</td>
<td>22</td>
<td>30</td>
<td>632</td>
<td>76</td>
</tr>
<tr>
<td>Polyacrylate</td>
<td>45</td>
<td>0</td>
<td>1.236</td>
<td>90</td>
</tr>
<tr>
<td>Polyacrylate</td>
<td>45</td>
<td>30</td>
<td>439</td>
<td>80</td>
</tr>
</tbody>
</table>

5.1.2 pH

The effect of EHD on the detackification of polyacrylate was tested at four pHs, 5, 7, 9, and 10, which covers the operational ranges of most recycled paper mills. Tack was almost equally reduced for all of the polyacrylates at pH 5, 7, and 9. The tack was even further reduced for the polyacrylate sample that was subjected to EHD at a pH of 10. This indicates that EHD can be effective under most recycled paper pH conditions.

The results are shown in Table 9.

Table 9. The effect of pH on the tack of EHD treated polyacrylate films.

<table>
<thead>
<tr>
<th>Type</th>
<th>pH</th>
<th>No. of Discharges</th>
<th>Tack (g/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyacrylate</td>
<td>5</td>
<td>0</td>
<td>905</td>
</tr>
<tr>
<td>Polyacrylate</td>
<td>5</td>
<td>40</td>
<td>420</td>
</tr>
<tr>
<td>Polyacrylate</td>
<td>7</td>
<td>0</td>
<td>955</td>
</tr>
<tr>
<td>Polyacrylate</td>
<td>7</td>
<td>40</td>
<td>420</td>
</tr>
<tr>
<td>Polyacrylate</td>
<td>9</td>
<td>0</td>
<td>820</td>
</tr>
<tr>
<td>Polyacrylate</td>
<td>9</td>
<td>40</td>
<td>460</td>
</tr>
<tr>
<td>Polyacrylate</td>
<td>10</td>
<td>40</td>
<td>290</td>
</tr>
</tbody>
</table>

5.1.3 Fiber Consistency

The effect of EHD on the tack and hydrophobicity of polyacrylate in the presence of various consistencies of pulp was examined. There is a significant tack reduction and decrease in hydrophobicity for polyacrylates that were subjected to EHD in the presence of pulp at 0.5% and 1.0% consistency pulp. There is a notable decrease in tack for the polyacrylate stickie in 3.5% pulp, however, the hydrophobicity did not significantly
change, potentially due to some fiber on the stickie surface. These results are shown in Table 10.

Table 10. The effect of fiber consistency on the tack and hydrophobicity of EHD treated polyacrylate films.

<table>
<thead>
<tr>
<th>Type</th>
<th>Fiber Consistency</th>
<th>No. of Discharges</th>
<th>Tack (g/cm²)</th>
<th>Hydrophobicity (degrees)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyacrylate</td>
<td>3.50%</td>
<td>0</td>
<td>645</td>
<td>82</td>
</tr>
<tr>
<td>Polyacrylate</td>
<td>0.50%</td>
<td>40</td>
<td>400</td>
<td>73</td>
</tr>
<tr>
<td>Polyacrylate</td>
<td>1.00%</td>
<td>40</td>
<td>405</td>
<td>78</td>
</tr>
<tr>
<td>Polyacrylate</td>
<td>3.50%</td>
<td>40</td>
<td>495</td>
<td>81</td>
</tr>
</tbody>
</table>

5.1.4 Chemical Additives

The effect of EHD on the tack and hydrophobicity of polyacrylates in the presence of commonly used paper machine wet end chemicals was also examined. The tack of polyacrylate in the presence of DADMAC was significantly reduced. The hydrophobicity of polyacrylates in the presence of retention aid and surfactant was slightly reduced, however the control hydrophobicities were initially low, due to the partially hydrophilic nature of both the retention aid and surfactant.

Table 11. The effect of chemical additives on the tack and hydrophobicity of EHD treated polyacrylate films.

<table>
<thead>
<tr>
<th>Type</th>
<th>Additive</th>
<th>No. of Discharges</th>
<th>Tack (g/cm²)</th>
<th>Hydrophobicity (degrees)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyacrylate</td>
<td></td>
<td>0</td>
<td>1,716</td>
<td>Not Tested</td>
</tr>
<tr>
<td>Polyacrylate</td>
<td>DADMAC (100 ppm)</td>
<td>10</td>
<td>518</td>
<td>Not Tested</td>
</tr>
<tr>
<td>Polyacrylate</td>
<td>Retention aid (100 ppm)</td>
<td>0</td>
<td>Not Tested</td>
<td>79</td>
</tr>
<tr>
<td>Polyacrylate</td>
<td>DADMAC (100 ppm)</td>
<td>40</td>
<td>Not Tested</td>
<td>76</td>
</tr>
<tr>
<td>Polyacrylate</td>
<td>Surfactant (100 ppm)</td>
<td>0</td>
<td>Not Tested</td>
<td>81</td>
</tr>
<tr>
<td>Polyacrylate</td>
<td>Surfactant (100 ppm)</td>
<td>40</td>
<td>Not Tested</td>
<td>78</td>
</tr>
</tbody>
</table>

5.1.5 Distance Studies

The effect of the distance from EHD source on stickie detackification, hydrophobicity, and ferrous sulfate oxidation was also studied. Polyacrylate films subjected to EHD had decreased tack and hydrophobicity 10cm, 50cm, and 1.5m from the EHD source, which is shown in Table 12. Additionally, ferrous sulfate that was
subjected to EHD up to 4.5m from the EHD source showed some oxidation. These results are shown in Figure 35.

Table 12. The tack and hydrophobicity of polyacrylate films subjected to EHD treatment at different distances from EHD source.

<table>
<thead>
<tr>
<th>Type of Stickie</th>
<th>Distance from EHD source</th>
<th>No. of Discharges</th>
<th>Tack (g/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyacrylate</td>
<td>Control</td>
<td>0</td>
<td>1,225</td>
</tr>
<tr>
<td>Polyacrylate</td>
<td>10cm</td>
<td>30</td>
<td>605</td>
</tr>
<tr>
<td>Polyacrylate</td>
<td>13cm</td>
<td>60</td>
<td>864</td>
</tr>
<tr>
<td>Polyacrylate</td>
<td>50cm</td>
<td>30</td>
<td>552</td>
</tr>
<tr>
<td>Polyacrylate</td>
<td>1.5m</td>
<td>60</td>
<td>714</td>
</tr>
</tbody>
</table>

Figure 35. The effect of EHD on ferrous sulfate oxidation as a function of distance.

5.2 Stickie Screenability

Since EHD modified the surface of the stickie, an experiment was performed to determine whether the screenability of a stickie would be effected by EHD. Accordingly, the polyacrylate stickie was homogenized, suspended in water to form a 1% suspension, and subjected to EHD. The results, shown in Figure 36, demonstrate that the rejects (as measured with a 150μm screen) increased significantly after 20 exposures to EHD. The
oxidation of the stickie surface appears to make it less likely to deform through removal screens. The standard deviation was 2.0%.

Figure 36. Effect of EHD on polyacrylate screenability.

5.3 Mill Trial

The EHD trial was performed at the VISY Papermill in Conyers, Georgia from April 28, 2000 to June 1, 2000. The EHD submersible electrode assembly was placed in the top liner stuff box, which has a flow rate of about 6000 liters per minute and a pulp consistency of about 3.5%. The average residence time was 10 seconds based on the stuff box capacity of 1000L. The stuff box and headbox pH is usually 7.0-7.2.

The tack of the mill stickies before and after EHD treatment was quantified by a colloidal stickie measurement developed and performed by Sung9. Pulp samples from the top ply headbox were collected and filtered. The filtrate was then concentrated and applied as a thin film to a metal coupon. The tack was then measured using a Polyken tack tester. The tack of the mill stickies decreased over the treatment time. When the EHD unit was turned off for a few days, the tack values recorded were much higher. The
mill qualitatively tracked the amount of stickie build-up on the dryer fabric as well as the amount of time required to clean the felt. The mill reported that the amount of deposited stickies did not change. The felts, however, were reported as being easier to clean, perhaps saving up to one hour of clean up time, compared to clean up before the EHD trial. The tack is illustrated in Figure 37. Figure 37 also shows the days that the EHD unit was operating and clean up days. The clean up days are represented by asterisks in Figure 37.

![Figure 37. The tack of mill stickies during the EHD mill trial.](image)

5.4 Major Findings and Discussion

The major findings of the applications based studies were that EHD decreased the tack and hydrophobicity of polyacrylate film on coupons under the operating conditions of most recycled paper mills. Polyacrylate tack and hydrophobicity decreased when subjected to EHD in temperatures from 15°C to 45°C, with the largest tack decrease from
EHD treated polyacrylate at 45°C, which is a common operating temperature. At higher temperatures, the polymer chain is more mobile, potentially increasing the surface area, which would increase the amount of stickie surface available for EHD initiated oxidation. The polyacrylate tack also decreased when subjected to EHD at pH of 5 to 10, with the largest tack decrease from EHD treated polyacrylate at a pH of 10.

Polyacrylate stickies had decreases in tack and hydrophobicity when subjected to EHD in the presence of varying consistencies of pulp. The tack results were similar for polyacrylate stickies subjected to EHD in 0.5% and 1.0% consistency pulp. However, EHD was less effective in the presence of 3.5% consistency pulp. This is probably due to the pulp absorbing some of the shock wave, resulting in less cavitation, and also the pulp potentially competing for hydroxyl radicals.

Polyacrylate stickies that were subjected to EHD in the presence of DADMAC, a common detackifying additive, also showed a reduction in tack. Exposure to EHD without DADMAC decreases the tack of polyacrylates substantially more than DADMAC alone, suggesting that EHD could replace DADMAC as a stickie control method. Polyacrylate stickies that were subjected to EHD in the presence of retention aid and surfactant showed no further decreases in hydrophobicity compared to the control. This is most likely due to the retention aid and surfactant covering the surface of the stickie before EHD treatment. Retention aids and surfactants have hydrophilic ends, which most likely were oriented away from the stickie surface, resulting in an apparent decrease in hydrophobicity.

Distance studies revealed that there is a relationship between tack reduction and distance from EHD source. However, there is still a decrease in tack up to 1.5m and
there is some free radical formation up to 4.5m from the EHD source, indicating that one
EHD unit could potentially treat large volumes of white water or pulp slurry.

Stickie screenability studies showed that after 20 exposures to EHD the amount of
rejected stickies increased significantly, suggesting that the stickies were somewhat
hardened by EHD treatment. However, the amount of rejected stickies did not increase
after 20 EHD exposures. This is probably due to the stickies tested, which had a size
range of 1μm to 1000μm. Since the hole screen size was 150μm, only stickies that were
larger than 150μm would have been screened out.

The applications studies were performed in order to determine potential locations
for optimal placement in a recycled paper mill. From the applications studies, the EHD
unit can be placed in most temperature, pH, and fiber consistency conditions. Potential
locations include white water chests. This could be in the stuff box at higher consistency
or following the fan pump, where the pulp slurry is usually at headbox consistency.

The EHD trial at VISY Paper was conducted over a five-week period. The mill
staff selected stuff box placement because it had an opening in the top where the EHD
submersible unit could be easily installed. The stuff box provided 10 seconds of average
residence time. The stickie tack did decrease over the time of the trial. Stickie tack
increased when the EHD unit was not operating. The mill staff also reported that the felts
were easier to clean during the trial, compared to pre-trial cleanings. This could be
explained by the decrease in tack. Stickies that are less tacky could require less chemical
and mechanical cleaning, thus decreasing clean up time. However, the amount of stickie
build-up on the dryer felts seemed to be the same. This is probably due to the fact that
the stickies are still hydrophobic; therefore, the hydrophobic effect will provide attraction
for stickies to other deposited stickies and machine surfaces, like the dryer felts.

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Given the results of the mill trial, EHD treatment can be beneficial for recycle paper mills. Decreases in cleaning time can reduce the amount of downtime, allowing for a quicker startup and increased production. The decrease in the amount of cleaning chemicals would lead to some cost savings. More importantly, less chemical use and mechanical cleaning would have the added benefit of increasing the useful life of dryer felts.
CHAPTER 6. SUMMARY AND RECOMMENDATIONS FOR FUTURE WORK

6.1 Summary

In summary, exposure of stickie surfaces to electrohydraulic discharge (EHD) leads to decreases in tack and hydrophobicity. The exposure of stickies to EHD also leads to their oxidation, most likely by free radicals generated by the acoustic field. The incorporation of oxygen into the surface and the decreases in pH and hydrophobicity make a strong case for the involvement of the hydroxyl radical. The unique attribute of this technique is that it efficiently generates hydroxyl radicals throughout a large volume, which makes it suitable for recycled pulp and paper applications.

6.2 Recommendations For Future Work

The first mill trial revealed many of the future recommendations for the continuation of this research project. There are ongoing opportunities in the area because there are two confirmed mill trials for the fall of 2000. The first recommendation is that quantifiable metrics be defined and measured throughout the trial. Also, there should be pre-trial and post-trial data collected in order to determine if EHD treatment had a significant effect on the metric in question. On a practical level, the mill should be invested in the outcome of the trial, meaning their engineers and operators should be involved on all levels of the trial.

Future trials should also consider EHD placement in the white water chest, since it appeared from the mill trial that colloidal stickies associated with the white water were detackified during EHD operation. The EHD unit could potentially treat more white water stickies in a large tank without competition from fiber. Also, thin stock placement could be investigated.

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Finally, other pulp and paper applications have presented themselves over the course of this EHD research. One in particular is the potential for speeding up the reactions of hydrogen peroxide with fiber during bleaching. Another aspect that could be explored is the potential for removing scale on surfaces that are submerged in water, such as pipes. There may be many undiscovered uses for EHD that could potentially benefit the pulp and paper and allied industries.

6.3 Acknowledgements

There were too many people that were instrumental in my educational experience at IPST to mention here, but I will point out a few that were really important to me. I would first like to thank IPST and its member companies for their support and the opportunity to pursue the Ph.D. degree. I would also like to thank the DOE for partial financial support of this project, Dave Kosboth and his staff at VISY Paper for allowing an EHD trial in their mill, and Lisa Detter-Hoskin for performing the XPS analysis.

I would like to thank my advisor, Dr. Banerjee, for his ongoing support and for teaching me how to recognize the hidden opportunities that exist within research.

I would like to also thank Steve Makris and Mario Zaltzman who have challenged me throughout my Ph.D. education and in my life. Additionally, I thank Greg and Melissa Fike for their editing and for keeping me focused. I give special thanks to Mr. Woody Rice for being an excellent mentor and role model in this ever challenging paper industry.

I gratefully thank my wife, parents, and family for believing in me and providing me with a genuine respect for higher education. It is through their support and love that I know that anything is possible.
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APPENDIX I. STATISTICS

1.1 Tack

The tack uncertainty was determined by measuring the tack at five different locations on a polyacrylate film that was on a metal coupon. The results are listed in Table 13. The standard deviation was 63.2.

Table 13. Tack statistics for polyacrylate stickie film.

<table>
<thead>
<tr>
<th>Location</th>
<th>Tack (g/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1127</td>
</tr>
<tr>
<td>2</td>
<td>1281</td>
</tr>
<tr>
<td>3</td>
<td>1260</td>
</tr>
<tr>
<td>4</td>
<td>1197</td>
</tr>
<tr>
<td>5</td>
<td>1253</td>
</tr>
<tr>
<td>Mean</td>
<td>1223.6</td>
</tr>
<tr>
<td>SD</td>
<td>62.3</td>
</tr>
</tbody>
</table>

1.2 Water Drop Contact Angle

The water drop contact angle uncertainty was determined by measuring the water drop contact angle at five different locations on a polyacrylate film that was on a metal coupon. The results are listed in Table 14. The standard deviation was 2.0.

Table 14. Water Drop Contact Angle statistics for polyacrylate stickie film.

<table>
<thead>
<tr>
<th>Location</th>
<th>Water Drop Contact Angle</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>83.2</td>
</tr>
<tr>
<td>2</td>
<td>81.9</td>
</tr>
<tr>
<td>3</td>
<td>82.6</td>
</tr>
<tr>
<td>4</td>
<td>78.2</td>
</tr>
<tr>
<td>5</td>
<td>80.7</td>
</tr>
<tr>
<td>Mean</td>
<td>81.3</td>
</tr>
<tr>
<td>SD</td>
<td>2.0</td>
</tr>
</tbody>
</table>

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1.3 X-Ray Photoelectron Spectroscopy (XPS)

The XPS experimental uncertainty was determined by coating a metal surface with a film of polyacrylate, drying it, and analyzing five different regions by XPS. The results are listed in Table 15. The standard deviation was 0.01.

Table 15. XPS statistics for polyacrylate stickie film.

<table>
<thead>
<tr>
<th>Location</th>
<th>C</th>
<th>O</th>
<th>Si</th>
<th>O/C</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>69.7</td>
<td>23.7</td>
<td>6.6</td>
<td>0.34</td>
</tr>
<tr>
<td>2</td>
<td>72.6</td>
<td>23</td>
<td>4.4</td>
<td>0.317</td>
</tr>
<tr>
<td>3</td>
<td>72.3</td>
<td>23</td>
<td>4.7</td>
<td>0.318</td>
</tr>
<tr>
<td>4</td>
<td>71.2</td>
<td>22.6</td>
<td>6.2</td>
<td>0.317</td>
</tr>
<tr>
<td>5</td>
<td>72.7</td>
<td>23.3</td>
<td>3.9</td>
<td>0.32</td>
</tr>
<tr>
<td>Mean</td>
<td>72</td>
<td>23.1</td>
<td>5</td>
<td>0.32</td>
</tr>
<tr>
<td>SD</td>
<td>1</td>
<td>0.4</td>
<td>1</td>
<td>0.01</td>
</tr>
</tbody>
</table>
APPENDIX II. PATENT

SYSTEM AND METHOD FOR ALTERING THE TACK OF MATERIALS USING AN ELECTROHYDRAULIC DISCHARGE

INVENTORS:
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SUJIT BANERJEE

CROSS REFERENCE TO RELATED APPLICATIONS
This application claims the benefit of U.S. Provisional Application Serial No. 60/134,284, filed May 14, 1999, which is incorporated herein by reference.

GOVERNMENT INTEREST
This invention was made with Government support under Contract No. DE-FC36-996010381, awarded by the Department of Energy. The Government has certain rights in this Invention.

FIELD OF THE INVENTION
The present invention generally relates to the art of controlling the tack of materials, and more particularly pertains to altering the tack of polymers used as adhesives and pitch.
BACKGROUND OF THE INVENTION

People throughout our society have become increasingly aware and concerned about the environmental issues that plague the world. The depletion of the ozone layer, the rain forests, and clean water are just a few of the environmental issues that are being addressed. One approach in addressing these issues includes preserving resources by recycling them. Consequently, the recycling industry has become instrumental to serving this need.

In the recycling field, one area of increasing interest is the reuse of wastepaper. Millions of tons of wastepaper are generated every year in the United States. Recycling this wastepaper can save countless trees, as well as provide other ecological and economic benefits. However, the key to reuse of this wastepaper is the removal of contaminants from the wastepaper, thereby facilitating the use of recycled or secondary fibers from the wastepaper.

The paper recycling industry encounters a variety of contaminants in wastepaper. Many of these contaminants adhere to paper fibers and therefore may cause problems during the recycling process. One such contaminant is "stickies", which were used originally as paper adhesives or tacky adhesives. Stickies typically are classified as hot melts, pressure-sensitive adhesives (PSAs), latexes, and binders. Pitch is another contaminant associated with both virgin and secondary fibers. Pitch is a part of the extractives from wood, and is released during pulping.

Contaminants may cause operational and product quality problems. Specifically, contaminants may be deposited on wires, felts, press rolls, and drying cylinders of paper machines. In addition, contaminants may hinder bonding of fibers, increase web breaks, and reduce product quality in the
papermaking process. Consequently, contaminants must be controlled in order to improve papermaking operations and product quality.

Tack is the sticky property of paper adhesives, paperboard adhesives and glue coating materials. The tack of an adhesive and the adhesive’s ability to bond to another surface is dependent, in part, upon the surface energy of the adhesive. Reducing the tack of contaminants can minimize the propensity of the contaminants to attach to paper machine surfaces, thereby leading to fewer operational problems.

Various prior art methods are used to reduce the tack of the contaminants. Some methods use repulpable or recyclable adhesives. More common methods include chemical additives for modification, detackification, or pacification of the contaminants. For instance, detackification of contaminants is frequently accomplished by adding minerals, such as talc, or surface-active chemicals. These minerals and surface-active chemicals attach to the surface of the contaminants and alter their surface properties, thereby causing tack reduction. This method of tack reduction is described in a publication entitled, “Successful Approach in Avoiding Stickies,” by S. Abraham, Tappi J., 81:2 79-84 (1998), which is incorporated herein by reference. Nonetheless, chemical additives can be very expensive and may cause other problems in the papermaking process, such as a decline in product quality.

Mechanical methods for controlling contaminants include dispersion, screening and cleaning. Dispersion is a technique by which contaminants are broken up into smaller and smaller particles until they are invisible in the final product. Unfortunately, the overall appearance of a product may be diminished greatly by the presence of contaminants. In
addition, when the product containing contaminants is wound, sticking may occur between adjacent layers.

Screens and centrifugal cleaners are typically used to remove stickies, pitch and debris from the fiber stream. In general, screens are used to physically separate fiber from contaminants based on the differences between the sizes and shapes of contaminants and the holes or slots in the screen. One problem is that screens cannot remove contaminants that are either smaller than the size of the screen hole or deformable enough to pass through the screen hole. Centrifugal cleaners separate contaminants from fiber primarily on differences between the specific gravities of the fiber and the contaminant. However, separation is poor if the specific gravity of the contaminant is similar to the specific gravity of the fiber.

Therefore, there is a need for a system and method for improving the removal efficiency of contaminants, such as stickies and pitch, from a fiber stream. In addition, there is a need for a system and method that can detackify contaminants by altering, without the use of chemicals, the surface properties of the contaminants. There is yet another need for a system and method that alters the tack of materials inexpensively and simply.

**SUMMARY OF THE INVENTION**

The present invention solves the above-described needs by providing a system and method for altering the tack of a material by the exposing the material to an electrical discharge in a liquid medium. In one aspect, the present invention provides a method for altering the tack of a material by immersing a material in a liquid medium and introducing an electrical discharge in the liquid medium, wherein the material is exposed to the electrical discharge and the electrical discharge causes a reduction in the
tack of the material. The exposure to an electrical discharge or spark can be repeated until the tack of the material is reduced to a desired level of tackiness.

The liquid medium is typically selected from a group consisting of whitewater, water, and a pulp slurry. The material is preferably a polymer used as an adhesive or the material may also be pitch. The polymer is selected from a group consisting of pressure sensitive adhesives, hot melts, latexes, and binders. Stickies or pitch may be suspended alone or attached to a surface of an object, such as a fiber, a metal object, a plastic object, and other machine surfaces. Moreover, the electrical discharge produces energy of about 0.1 to 25 kJ.

In another aspect, a method for reducing the tack of a contaminant in a liquid medium is described. Specifically, a high voltage/high current store of energy is discharged in a liquid medium containing a contaminant, wherein the energy is discharged in a predetermined time period and the energy causes the tack of the contaminant to be reduced.

In addition, multiple high voltage/high current stores of energy can be discharged in the liquid medium containing the contaminant until the tack of the contaminant reaches a desired level. The multiple high voltage/high current stores of energy may discharged from the same energy source or from different energy sources. In the case of multiple stores of energy emanating from different energy sources, the multiple high voltage/high current stores of energy may be discharged either synchronously or asynchronously. The energy is discharged from a sparker.

The predetermined time period preferably ranges from about 5 microseconds to 500 microseconds. The high voltage is preferably in the
range of about 500 V to 20,000 V. The high current is preferably in the range of about 10,000 A to 100,000 A.

In another aspect, a system for altering the tack of sticky contaminants in paper machine and pulp recycling operations so as to improve paper product quality in paper-making processes and to reduce operational problems is described comprising: a power supply supplying high current/high voltage electricity to a capacitor bank, where the capacitor bank is connected to the power supply and stores the high current/high voltage electricity supplied by the power supply; a chamber containing a liquid medium with sticky contaminants; and at least one pair of electrodes being submersed in the liquid medium contained in the chamber, where the at least one pair of electrodes is cabled to the capacitor bank and releases in the liquid medium at least one spark of the high current/high voltage electricity stored in the capacitor bank, wherein the sticky contaminants in the liquid medium are exposed to the release of the high current/high voltage electricity from the at least one pair of electrodes, thereby altering the tack of the sticky contaminants.

The release of high current/high voltage electricity produces energy of preferably about 0.1 to 25 kJ. Moreover, the duration of the release of high current/high voltage electricity ranges from preferably about 5 microseconds to 500 microseconds.

These and other objects, features, and advantages of the present invention may be more clearly understood and appreciated from a review of the following detailed description of the disclosed embodiments and by reference to the appended drawings and claims.
**BRIEF DESCRIPTION OF THE DRAWINGS**

Fig. 1 illustrates a system for reducing the tackiness of a material consistent with an embodiment of the present invention.

Fig. 2 illustrates an exemplary operating environment consistent with an embodiment of the present invention.

Fig. 3 illustrates another exemplary operating environment consistent with an embodiment of the present invention.

Fig. 4 is a graph illustrating the effects of sparking on tack of stickies under various experimental conditions in accordance with an embodiment of the present invention.

Fig. 5 is a graph illustrating the effects of sparking on tack of stickies under various experimental conditions in accordance with an embodiment of the present invention.

Figs. 6a and 6b illustrate the effects of sparking on stickie screenability in accordance with an embodiment of the present invention.

Fig. 7 is a graph illustrating the effect of sparking on tack of pitch in accordance with an embodiment of the present invention.

**DETAILED DESCRIPTION**

Polymers used as adhesives, such as stickies, and pitch are commonly found in whitewater and pulp slurries. Consequently, these contaminants due to their sticky property, known as tack, can attach to components of a paper machine, thereby causing operational problems. These contaminants may also reduce product quality when present in a final product produced by the paper machine. Hence, it is desirable to reduce the tack of these materials in the whitewater or pulp slurry to ameliorate the removal of these contaminants from the fiber stream, to eliminate the negative effects they
have on product quality when present in the final product, and to reduce operational problems. By doing so, the whitewater or pulp slurry can be efficiently used in the papermaking process.

In general, the present invention provides a system and method for altering the tack of a material, which in turn, improves the removal efficiency of the materials or contaminants from a liquid medium, diminishes the negative effects of tackiness the contaminants may have on the final product, and reduces papermaking operational problems. It has been found by those skilled in the art that a material becomes less tacky by changing the surface energy of the material.

While prior art methods use techniques for altering the tackiness of materials by using chemical additives, the present invention does not require chemicals for this purpose. Specifically, the present invention changes the surface energy of a material by exposing the material for a short duration to low-energy pulsed electrical discharges between a pair of electrodes that are submerged in a liquid medium. The result is a detackified or less tacky material, which improves removability of the contaminant from a liquid medium, such as a fiber stream, and reduces papermaking operational and process problems.

As used herein, the terms “material” and “contaminant” are used interchangeably and specifically refer to polymers and pitch.

Exemplary embodiments of the present invention are described herein below in connection with Figs. 1-7, wherein like numerals represent like elements among the figures, and the accompanying examples.

Referring to Fig. 1, a system for reducing the tackiness of a material consistent with an embodiment of the present invention is shown. The system 10 includes a chamber 30 for housing a liquid medium, and a
sparking device, comprising a power supply 15, a capacitor bank 20, and a pair of electrodes or sparker 25. A sparking device that can be used in the present invention is the Sparktec plasma sparker (SPK-8000), which is manufactured and sold by Sparktec Environmental of Stoney Creek, Ontario, Canada.

Specifically, the pair of submersible electrodes or sparker 25 is cabled to a bank of capacitors housed in the capacitor bank 20. The sparker 25 releases the energy stored by the capacitors and may be placed in the chamber 30 containing a liquid medium 35. Alternatively, the sparker 25 may be positioned in a tank or other container, as shown in connection with Fig. 2, or in pipes through which the liquid medium flows, as shown in connection with Fig. 3. The sparker 25 may include a feeding mechanism (not shown), which ensures that the gap between the electrodes remains constant.

The power supply 15 controls power management and is functionally connected to the capacitor bank 20 for providing a constant current power supply to the capacitor bank 20. The power supply 15 may include a computer interface, which monitors the supply unit, controls the electrode feed mechanism, if present, and times the high voltage/high current discharge pulse generated by the bank of capacitors.

The capacitor bank 20 contains a bank of high voltage discharge capacitors for storing energy. The capacitor bank 20 may include a switch mechanism (not shown), which triggers the release of a high voltage/high current pulse to the sparker 25.

It will be appreciated by those skilled in the art that the present invention may include any suitable power supply capable of controlling power management and converting AC current to high DC voltages. It is
further appreciated that the present invention may utilize any pair of electrodes suitable for releasing high voltage/high current energy and capable of being properly secured such that the gap between the electrodes remains constant. For example, a pair of electrodes may be securely clamped or welded to a chamber or an air compressor may be used to ensure that the gap between the electrodes remains constant.

Referring to Fig. 1, the system 10 operates by injecting energy into a liquid medium 35 through a plasma channel formed by a high-current/high-voltage electrical discharge between the two submerged electrodes 25. The system 10 works on the same principle as a spark plug.

Specifically, a high voltage and a high current are impressed between the pair of electrodes 25, also referred to herein as a sparker 25, for a very short duration such that the energy dissipates by sonic/ultrasonic waves (also referred to as shock waves) that break up the water molecules. Consequently, the water molecules closest to the spark break up due in part to the spark itself, while the water molecules at some distance from the spark break up due to the sound waves caused by the spark. The electrohydraulic discharge or spark also produces ultraviolet and other radiation and generates reactive chemical species, such as hydroxyl radicals and other oxidants. As used herein, the terms “electrical discharge” and “electrohydraulic discharge” are used interchangeably, where electrohydraulic discharge means an electrical discharge that takes place in a liquid medium.

In the present invention, the high voltage used is preferably in the range of 500 V to 20,000 V, and more preferably in the range of 2,000 V to 8,000 V. The high current used is preferably in a range of 10,000 A to 100,000 A, and even more preferably about 50,000 A. The duration of the
electrical discharge is preferably less than 1 second, and more preferably in the range of 5 microseconds to 500 microseconds, and even more preferably about 150 microseconds.

When the sparker 25 is activated by supplying power from the power supply 15 to the capacitors in the capacitor bank 20, the capacitors are rapidly charged with electricity. At a predetermined interval, a process controlled high voltage/high current switch (not shown) associated with the capacitor bank 20 releases the stored energy from the capacitors to the electrodes 25 located in the chamber 30 containing the liquid medium 35. The high voltage/high current released from the capacitors then bridges the gap at the electrodes 25 causing the spark. Each spark preferably has energies ranging from 0.1kJ to 25kJ, and more preferably about 12kJ.

With continuing reference to Fig. 1, the material 40 to be treated is placed in the liquid medium 35 surrounding the sparker 25, and the sparking device is activated, whereupon the surface energy of the material is altered by the effect of the spark transmitted through the liquid medium 35. In other words, the material 40 is exposed to the electrical discharge from the electrodes 25.

The exposure may be direct, where the contaminant is or almost is in direct contact with the electrical discharge of the sparker 25 due to the close proximity of the contaminant to the sparker 25. Alternatively, the exposure may be indirect since the surface energy of the contaminant can be affected at a distance from the spark.

After exposure to the electrical discharge, the material’s surface energy changes, thereby altering the tack of the material. Typically, the surface energy of the material increases after exposure to the electrical discharge. The material is exposed to at least one spark, but can be exposed
to multiple sparks. Those skilled in the art will understand that the surface energy of the material may either increase or decrease after exposure to the electrical discharge resulting in an alteration in the tack property.

The liquid medium can be whitewater, a pulp slurry, or other fiber stream, where paper fibers are suspended in the stream and are transported with the flow of the stream. The liquid medium may also be water, which may or may not contain a solution of chemicals, such as chlorite or sodium hypochlorite, or chemicals typically present in whitewater.

The material to be treated is preferably a polymer used as an adhesive, also known as "stickies". As previously described, stickies may be classified as hot melts, latexes, pressure sensitive adhesives (PSAs), and binders. Examples of stickies include, but are not limited to polyacrylate PSAs, polyvinyl acetate (PVAc) and polyurethane. The group of polymers used as adhesives is commonly known by those skilled in the art, and the present invention is not limited in any way as to its applicability to altering the tack of that group of polymers used as adhesives. In addition, the material to be treated may also be pitch, which is a natural component of wood that behaves like stickies and is found in virgin fiber, as well as secondary fiber. These materials, namely stickies and pitch, are oftentimes attached to the surface of an object, such as paper machine components, including felts, wires, press rolls, drying cylinders, and other surfaces of the paper machine. These materials may also attach to fibrous surfaces, including paper, paperboard, and the like.

Figs. 2 and 3 illustrate exemplary operating environments for reducing the tack of contaminants in whitewater and recycled pulp, respectively. As used herein, the term "recycled pulp" refers to a pulp slurry containing contaminants such as stickies, pitch, and/or other solids.
In Fig. 2, the operating environment 75 shows a whitewater tank 100, which contains contaminated whitewater, namely whitewater with stickies and/or pitch. In addition, Fig. 2 shows a sparking device 101 comprising a pair of electrodes 25, a capacitor bank 20, and a power supply 15. The sparking device 101 is positioned such that the electrodes 25 are submerged in the whitewater tank 100. In paper mill and recycling environments, the sparker may have dimensions of about 4 feet high, about 5 inches wide, and about 2.5 inches deep, like the sparker manufactured and sold by Sparktec Environmental of Stoney Creek, Ontario, Canada. Those skilled in the art will understand that the present invention is not limited to the aforementioned sparker, but may integrate a sparker meeting specified parameters in the tank.

In Fig. 2, the contaminated whitewater is repeatedly exposed to the electrical discharges of the sparker 25, as previously described in connection with Fig. 1, while in the whitewater tank 100 until it becomes less tacky. This treated whitewater 120 then flows through the pipe or channel 115 and effectively combines with pulp 125, which flows from a pulp reservoir 105. Next, the combined whitewater and pulp 130 continues its approach flow to the paper machine 110. Advantageously, the present invention reduces operational problems that occur due to sticky contaminants in the papermaking process.

It will be appreciated by one skilled in the art that the sparking device 101 is not limited to placement in the whitewater tank 100, but may be placed anywhere in the system for treatment of the whitewater prior to its approach flow to the paper machine 110.

Referring to Fig. 3, the sparking device 101 is integrated into the pipe or channel 115 in a recycled pulp environment 200. Specifically, the
sparking device 101 is positioned and secured between a recycled pulp tank 205 and screens 210. The recycled pulp tank 205 contains recycled pulp 220. As the recycled pulp 220 flows from the recycled pulp tank 205 to the screens 210, the pulp 220 is repeatedly exposed to the electrical discharges of the sparker 25.

As a result of exposure to the electrical discharge or spark, the surface energy of the sticky contaminants in the pulp is altered such that the tack of the stickies is reduced. The treated pulp then flows through the screens 210, which filter out the contaminants, and continues its approach flow to the paper machine. As previously mentioned, this process improves the removal efficiency of contaminants from the fiber stream as is shown in connection with Figs. 6a and 6b, which are described in greater detail herein below.

It is preferable that the sparker is positioned as early in the flow process as possible. However, it will be appreciated by one skilled in the art that the sparker 25 may be positioned anywhere in the system as long as the pulp is treated before the pulp flows to the paper machine 110. Moreover, one skilled in the art will understand that direct exposure or contact with the electrical discharge from the electrodes is unnecessary due to the fact that the surface energy of the material may be altered a distance upstream or downstream from the location of the electrical discharge.

The present invention is not limited to the use of one sparker for the treatment of contaminated whitewater, pulp slurries, or other liquid media. Multiple sparkers may be used to reduce the tack of contaminants. The sparkers may discharge at different times or at the same time. The sparkers may be arranged such that each has its own capacitor bank and power supply. Alternatively, the sparkers may share a common capacitor bank and/or power supply. Also, at least one sparker may be placed directly in a
tank containing the whitewater, pulp slurry or other liquid media, instead of or in addition to placing the sparker along the pipe or channel through which the liquid medium containing the contaminants flows. As previously described, the present invention is not limited to uses with whitewater and pulp slurries, but may also include other liquid media containing polymers used as adhesives and/or pitch.

Advantageously, the present invention is an inexpensive system and method for altering the tack of materials. The inventive system is simple to implement and provides an economic benefit of reducing the tack of materials without using chemicals, which can be very expensive. However, the inventive system may be used in conjunction with use of conventional chemicals to further improve de tackification, while reducing the amount of chemicals typically required for such purposes.

The following examples, which are merely illustrative of the present invention, further demonstrate applications of the present invention in altering the surface energy of a polymer, as well as demonstrate the benefits associated therewith.

Example 1

Two 316 stainless steel coupons (5.5 cm²) were coated with 10 mL of an acrylate pressure sensitive adhesive (Carbotac latex from B.F.Goodrich), and dried so that the acrylate formed a thin, tacky surface film. One coupon was submerged in water in a thirty-gallon tank and treated with thirty sparks delivered with the sparker device. The surface energy of the film was measured before and after sparking. Surface energy is a measure of tack. Before treatment by the sparker, the surface energy was 15.7 dy/cm, whereas after treatment by the sparker, the surface energy was
22.9 dy/cm. These results demonstrate a substantial increase in surface energy upon spark treatment, where an increase in surface energy of the film indicates a reduction in tack.

Example 2

Stainless steel coupons (5.5 cm²) were coated with 10 mL of an acrylate pressure sensitive adhesive (Carbotac latex from B.F.Goodrich), and dried so that the acrylate formed a thin, tacky, surface film. These coupons were submerged in water in a three-gallon tank, and treated with sparks delivered with the sparking device. The results listed in Table 1 demonstrate that sparking induces an increase in surface energy, and that the tack decreases upon sparking. In this instance, tack is defined as the force required to remove a 1" diameter 305 stainless steel probe from the surface of the film as measured by a commercially available instrument manufactured by Instron of Canton, MA. One measurement was also made where the stickie was applied to a piece of blotting paper prior to sparking. The surface energy of the stickie film was also elevated, indicating that detackification did not require the stickie to have a hard base, but was also effective when it was deposited on fiber.

<table>
<thead>
<tr>
<th>conditions</th>
<th>sparks</th>
<th>Surface energy (dynes/cm)</th>
<th>tack (psi)</th>
</tr>
</thead>
<tbody>
<tr>
<td>control</td>
<td>0</td>
<td>17.4</td>
<td>20.6</td>
</tr>
<tr>
<td>sparked in water</td>
<td>10</td>
<td>28.8</td>
<td>11.7</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>26.7</td>
<td>9.03</td>
</tr>
<tr>
<td>----------------</td>
<td>-----</td>
<td>------</td>
<td>------</td>
</tr>
<tr>
<td>sparked in water</td>
<td>60</td>
<td>27</td>
<td>9.78</td>
</tr>
<tr>
<td>sparked in whitewater</td>
<td>30</td>
<td>29.6</td>
<td>6.49</td>
</tr>
<tr>
<td>sparked in water in the presence of sodium hypochlorite</td>
<td>30</td>
<td>29.6</td>
<td>3.45</td>
</tr>
</tbody>
</table>

**Example 3**

Experiments were also conducted in the presence of a small amount of sodium hypochlorite (1.4 g/L) dissolved in the water. In the presence of sodium hypochlorite, the surface energy of the stickie increased to an extent greater than the surface energy increase realized with the same number of sparks in the absence of the sodium hypochlorite. An attendant decrease in tack was also realized. It is speculated that one reason for this outcome is the alteration of sodium hypochlorite by the spark, thereby causing it to dissociate into active species, which then interacted with the polymer.

**Example 4**

Experiments were also conducted where the metal coupon was submerged in paper mill whitewater. The surface energy of the stickie increased to an extent greater than the surface energy increase realized with the same number of sparks in the presence of water alone. An attendant decrease in tack also occurred.

Both the sodium hypochlorite and the whitewater experiment demonstrate that components present in or added to water may induce a
degree of detackification additional to that anticipated by sparking in water alone.

Example 5

Fig. 4 is a graph illustrating the reductions of tack on PSAs. All PSA samples were polyacrylate films on metal coupons. Samples were sparked in water thirty times, sixty times, both toward the spark, and thirty times turned away from the spark. Each shows similar tack reductions in comparison with a control, which was placed in water, but not sparked. Other samples were sparked thirty times in whitewater from a recycle mill and thirty times in 500-ppm hypochlorite solution in water. Both samples showed decreases in tack compared to the regular water control sample and the hypochlorite control, which was placed in the 500-ppm hypochlorite solution, but not sparked.

Example 6

Fig. 5 is a graph illustrating the reductions of tack on PSAs in the presence of bleached Kraft pulp in water at various consistencies. All PSA samples were polyacrylate films on metal coupons. The tack was reduced for PSAs sparked forty times in 0.5, 1.0, and 3.5 % consistency pulp (based on fiber/fiber + water) compared to the control which was placed in 3.5% consistency pulp in water, but not sparked.

Example 7

Figs. 6a and 6b illustrate the effect of sparking on screenability. PSA in Fig. 6a was emulsified in water to a 0.1 % consistency (PSA/PSA+water) solution, then the solution was then split into two equal
volumes. The reject amount of stickie PSA screened using a 150-micron PULMAC pressure-screening device, which is manufactured and sold by Pulmac of Montpelier, VT, increased 6% with sixty sparks compared to the control volume, which was screened but not sparked.

PSA in Fig. 6b was emulsified in water to a 0.1% consistency (PSA/PSA+water) solution and mixed with bleached Kraft pulp to achieve a 1% pelp consistency. Finally, the stickie-pulp-water solution was then split into two equal volumes. The reject amount of stickie PSA screened using a 150-micron PULMAC pressure-screening device increased 6% with eighty sparks compared to the control volume, which was screened but not sparked.

**Example 8**

Fig. 7 is a graph illustrating the effect of sparking on pitch. Pitch films on metal coupons were heated to 100°C and tested for tack using the Polyken Tack Tester manufactured and sold by Testing Machines Inc., Islandia, NY. Tack measurements were taken starting at 65°C and ending at 35°C. The results show that tack was reduced for the pitch samples that were sparked 100 times compared to the control, which was not sparked.

Alternative embodiments will become apparent to those skilled in the art to which the present invention pertains without departing from its spirit and scope. Accordingly, the scope of the present invention is defined by the appended claims rather than the foregoing description.
CLAIMS

What is claimed is:

1. A method for altering the tack of a material, comprising the steps of:
   (a) immersing a material having tack in a liquid medium; and
   (b) introducing an electrical discharge in the liquid medium, thereby exposing the material to the electrical discharge to cause a reduction in the tack of the material.

2. The method of Claim 1, further comprising the step of repeating step (b) until the tack of the material is reduced to a desired level of tackiness.

3. The method of Claim 1, wherein the liquid medium is selected from a group consisting of whitewater, water, and a pulp slurry.

4. The method of Claim 1, wherein the material is a polymer used as an adhesive.

5. The method of Claim 4, wherein the polymer is selected from a group consisting of pressure sensitive adhesives, hot melts, latexes, and binders.

6. The method of Claim 1, wherein the material is pitch.
7. The method of Claim 1, wherein the material is attached to a surface of an object.

8. The method of Claim 7, wherein the object is a paper fiber.

9. The method of Claim 7, wherein the object is a metal.

10. The method of Claim 7, wherein the object is a plastic.

11. The method of Claim 1, wherein the electrical discharge produces energy in the range about 0.1 kJ to about 25 kJ.

12. A method for reducing the tack of a contaminant in a liquid medium, comprising the step of:

   discharging in a predetermined time period a high voltage/high current store of energy in a liquid medium containing a contaminant having tack, thereby causing the tack of the contaminant to be reduced.

13. The method of Claim 12, further comprising the step of discharging multiple high voltage/high current stores of energy in the liquid medium until the tack of the contaminant is at a desired level of tackiness.

14. The method of Claim 13, wherein the multiple high voltage/high current stores of energy are discharged from a single sparker.
15. The method of Claim 13, wherein the multiple high voltage/high current stores of energy are discharged synchronously from multiple sparkers.

16. The method of Claim 13, wherein the multiple high voltage/high current stores of energy are discharged asynchronously from multiple sparkers.

17. The method of Claim 12, wherein the store of energy is discharged from a sparker.

18. The method of Claim 12, wherein the liquid medium is selected from a group consisting of whitewater, water, and a pulp slurry.

19. The method of Claim 12, wherein the contaminant is a polymer used as an adhesive.

20. The method of Claim 12, wherein the contaminant is attached to a surface of an object.

21. The method of Claim 20, wherein the object is a fibrous material.

22. The method of Claim 20, wherein the object is a paper machine component.
23. The method of Claim 12, wherein the contaminant is pitch.

24. The method of Claim 12, wherein the discharge of energy produces energy in the range of about 0.1 kJ to about 25 kJ.

25. The method of Claim 12, wherein the predetermined time period ranges from about 5 microseconds to about 500 microseconds.

26. The method of Claim 12, wherein the high voltage is in the range of about 500 V to about 20,000 V.

27. The method of Claim 12, wherein the high current is in the range of about 10,000 A to about 100,000 A.

28. A system for altering the tack of sticky contaminants in paper machine and pulp recycling operations so as to improve paper product quality in paper-making processes and to reduce operational problems, comprising:

   a power supply supplying high current/high voltage electricity to a capacitor bank, where the capacitor bank is connected to the power supply and stores the high current/high voltage electricity supplied by the power supply;

   a chamber containing a liquid medium with sticky contaminants; and

   at least one pair of electrodes being submersed in the liquid medium contained in the chamber, where the at least one pair of
electrodes is cabled to the capacitor bank and releases in the liquid medium at least one spark of the high current/high voltage electricity stored in the capacitor bank,

wherein the sticky contaminants in the liquid medium are exposed to the release of the high current/high voltage electricity from the at least one pair of electrodes, thereby altering the tack of the sticky contaminants.

29. The system of Claim 28, wherein the liquid medium is selected from a group consisting of whitewater, water, and a pulp slurry.

30. The system of Claim 28, wherein the liquid medium is a fiber stream, where paper fibers are suspended in the stream.

31. The system of Claim 28, wherein the sticky contaminants are stickies.

32. The system of Claim 28, wherein the sticky contaminants are pitch.

33. The system of Claim 28, wherein the sticky contaminants are a combination of stickies and pitch.

34. The system of Claim 28, wherein the sticky contaminants are attached to a surface of an object.
35. The system of Claim 28, wherein the at least one spark of the high current/high voltage electricity produces energy in the range of about 0.1 kJ to about 25 kJ.

36. The system of Claim 28, wherein the at least one spark of the high current/high voltage electricity has a duration of at least about 5 microseconds to about 500 microseconds.
SYSTEM AND METHOD FOR ALTERING THE TACK OF MATERIALS USING AN ELECTROHYDRAULIC DISCHARGE

ABSTRACT

A system and method for altering the tack of a material, namely a polymer used as an adhesive, also known as stickies, or pitch. The present invention reduces the tack of the stickies and pitch by exposing the materials for a short duration to low-energy pulsed electrical discharges between a pair of electrodes that are submerged in a liquid medium, such as a fiber stream, water, a pulp slurry, or whitewater.

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