Inks – Water-Based

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Introduction:

An ink is a liquid or a paste like (semi-liquid) material that is used for drawing, writing, and printing either text or graphics. There are many different types or rather methods of printing such as typographic, flexographic, lithographic, gravure, screen, and NIP or non-impact printing such as ink-jet printing. See figure one for the sales of different inks in the U.S. Ink is a colloidal system that is typically comprised of colorant, vehicle, solvent, and additives. Because of the many different applications or uses of ink a variety of types and formulations are necessary.

Composition of Inks:

The colorant can either be pigments, or dyestuffs. Pigments can be classified as organic pigments, inorganic pigments, metallic, florescent, pearlescent, etc., all of which are insoluble in the vehicle, where as dyestuffs are soluble in the vehicle. When referring to a pigment it is often done so by either their formula number, or their color index name. Pigments are used frequently in many of the printing applications, where as dyestuffs are more common in water-based inks such as those found in pens. All though more recently there have been inks that make use of both a dye and a pigment. An example of a dye is eosine which is commonly used in red fountain pens. Two inorganic pigments are titanium dioxide which is used in white inks, and carbon black which is used to make black inks. Organic pigments are used for colored inks; several examples are phtalocyanine pigments which give green and blue inks, and azo pigments for red and yellow inks. Over the past several decades health and environmental concerns have lead to the reduction of the use of inorganic color pigments as they would typically be or contain toxic heavy metals.[3]

The vehicle also called a binder or a varnish allows for the colorant to be in a printable form such that the colorant can reach the substrate or the surface which it is to affix itself to. Binders are part of the vehicle and are typically resins that will remain on the substrate or surface along with the colorant, sometimes the additives are also considered to be part of the binder, see figure two for a list of printing processes along with the binder used. Resins are polymeric materials with some example of synthetic resins being epoxy resins, polyamide resins, and acrylic resins.[3]

The solvent is used to dissolve the binder of the ink, and also to change the viscosity of the ink. Examples of solvents are xylene, toluene, mineral oil, alcohols, esters, ketones, and water, see figure two for a list of printing processes along with the solvent used. In most printing processes, and many of the ink formulations the solvent is removed by the drying of the ink. In some cases such as in UV-curing inks, the solvent will remain behind and become part of the binder.[3]

Additives are typically the smallest percentage of the composition of the ink. They are used to adjust the properties of the ink, or add a property to the ink thus increasing its performance. An ink may contain additives such as waxes, plasticizers, defoaming agents, thixotropy promoters, optical brighteners, anti-skinning agents, adhesion promoters, and driers.[3]

Water-Based Inks:

A water-based ink is an ink that has either the pigments or the dyes in a colloidal suspension in a solvent, with the solvent being water. All though the main solvent in water-based inks is water, there can also be other co-solvents present. These co-solvents typically are VOC's.

Water-based inks have been in existence since around 2500 B.C. The first water based inks were black writing inks that were typically carbon in water suspensions that were stabilized by either egg albumen or a natural gum.[5] Even though water-based inks have existed for over 4500 years; they were used very little up until the late 1960's. Water-based inks have inherent problems, and thus ignored as a viable option to other solvent based inks for some time. In the 1970's a crude oil shortage, combined with a new awareness of the damaging effects that the solvents in ink could have both on humans and the environment, new laws were put into effect forcing the ink industry to seek an alternative in the form of water-based inks.[11] The goal of using water-based inks is to completely remove hazardous chemical from ink, not just reduce the VOC's that are present.

Properties Used to Classify Inks:

When classifying or trying to determine what ink should be used for a given process or application some general properties are examined. Ink length which describes the inks viscosity, the inks tack or ability to adhere to surfaces, the fineness of the grind being the size of the particles, the color or color strength, drying time, rub resistance, and gloss. Determining whether or not a specific ink can be used for a given application may also depend on the odor that the ink may transfer to the substrate, the solvent that might remain, bleeding of the colorant, heat resistance, cold resistance, or any number of other properties.

Properties of Water-Based Inks:

As with all inks, water-based inks are formulated for their specific application and for specific properties or characteristics. That is the type of printing process they are to be used in, the substrate or surface they are to be printed on, the environment that the ink will be exposed to, the texture of the ink, the color of the ink, etc. The main properties of interest with water based inks are their viscosities, surface tensions, stability of the colloidal dispersion, size and shape of the colorant particles, shear stability, bleeding, foamability, scrubbing resistance, water resistance, boiling point, temperature, and the pH.[3]

The rheology of a system can be broken down into four categories, Newtonian, non-Newtonian (pseudoplastic), dilatant, and thixotropic. Newtonian flow is where viscosity will remain more or less constant as shear force is applied. Non-Newtonian flow or pseudoplastic flow is when viscosity will decrease as there is an increase in shear. Dilatant flow is when both the viscosity and shear increases together. Thixotropic flow is where the where viscosity will decrease as there is an increase in shear, which is similar to pseudoplastic flow with exception of thixotropic flow having a time dependent characteristic. Most water-based inks will fall into the category of thixotropic flow behavior. That is the ink will have a decreased viscosity when a shear force is applied, and when the shear force is removed the viscosity will return to its previous viscosity, see figure four.[11] In order to adjust the viscosity to the desired value a polymeric thickening agent can be used to increase the viscosity.

Surface tension of an ink affects properties such as the foaming of an ink, and an inks wettability. The wettability of an ink is the inks ability to coat a substrate or surface. An idealized coating, or the perfect ink will have a contact angel ? = 0, where cos? = (?$_s$ – ?$_{sl}$) / ?$_l$. In order for proper wetting of the substrate or surface the spreading coefficient S = (?$_s$ – ?$_{sl}$) – ?$_l$ must be positive. Generally speaking the higher the surface tension of the substrate the easier it will be to coat. Similarly, the lower the surface tension of the liquid that will be coating the substrate, the better it will wet. The best situation for the coating of a substrate occurs when the surface tension of the substrate is much greater then that of the liquid that will be coating the substrate. This is a problem for water-based inks, as water has a very high surface tension of 72 mN/m, where are most other solvent based inks have a surface tension between 20-35 mN/m, so the surface tension of the water-based ink will be higher then that of most substrates that it will be used to coat.[2] To solve this problem typically a surfactant will be added, or the surface of the substrate will be modified through cleaning or another process. Surfactants are so called "surface active" molecules that contain both a hydrophilic and a hydrophobic portion. The addition of a surfactant to a water-based ink will have the result of drastically lowering the surface tension of the ink due to the orientation effects at interfaces caused by the hydrophilic and hydrophobic portions of the surfactant. See figure five for a comparison of several substrate wetting additives and their effects on the properties of the ink, and see figure six for a graph and diagram of the effects of surfactants on surface tension. The addition of the surfactant has the effect of lowering the surface tension, but it also accelerates the formation of foams in the ink. To prevent this it is necessary to add an anti-foaming agent such as hydrophobic solids, or fatty acids.[3]

The colloidal stability of the ink is necessary to have quality printing, as well as to ensure a long shelf-life of the ink. With out stabilizing colloidal system of the ink, the pigment would settle with in a short time making the ink useless. There are two methods by which water-based inks can be stabilized, the addition of surfactants, and the addition of polymers, in some cases there the colloidal system is stabilized by both. The addition of surfactant and/or polymer to the water-based ink will result in the surfactant and/or polymer adsorbing at the solid (pigment)/liquid interface. The adsorbed surfactant and/or polymer will form coating on the pigment of various compositions and thicknesses which will result in a net repulsion of the pigment with in the ink causing its stabilization. The draw back of using a surfactant and/or polymer to stabilize the colloidal system will be the negative affects seen on the applicability of the ink and its color strength.[5]

The size and shape of the colorant particles are important in regards to the inks colorfastness, colloidal stability, viscosity, as well as many other properties. When pigments are used to color the ink it is necessary to choose the size and shape of the particles to meet the necessary requirements of the ink. The size of the particles of the pigment is important for colloidal stability, the smaller the particles are the easier it will be for the solution to stabilize, and also the smaller the particles are, the brighter or more pronounced the color will be, typical size distributions of particles of carbon black pigment can be seen in figure 7.

The temperature and pH of water-based inks must be monitored throughout the printing process, as even a small change in either can cause poor printing due to the change in the properties of the ink. A change in the pH or temperature of the ink will result in a change in the surface tension of the ink, the viscosity of the ink, as well as the colloidal stability of the ink, all of which are unwanted. The boiling point or heat of vaporization of the ink is an important factor in that it dictates the amount of time and the temperatures needed to dry or cure the ink. One of the difficulties of water based inks is due to water having a high heat of vaporization. In order for the ink to dry or cure it is necessary for all of the solvent to be removed, and due to water having a higher heat of vaporization as compared to similar solvents that are used in inks, the time and the temperatures necessary to dry or cure the ink is increased greatly.[7]

Through the use of additives many of the properties of the ink can be changed. Typically water-based inks are not water resistant or able to dry or cure quickly, this can be changed though by adding waxes to increase the inks water resistant property, or through the addition of a catalyst to accelerate the drying or curing. A problem with the addition of a catalyst to accelerate the drying or curing time is that the shelf life of the water-based ink is drastically reduced to around 12-24 hours.

Advantages and Disadvantages of Water-Based Ink:

Water-based inks were not widely used or accepted until the 1980's due to the many problems associated with them. Prior to the 1980's water-based inks were only used on porous surfaces such as paper or cardboard that required only minimal quality and detail in the prints. The use of water-based inks by printing companies required them to purchase new equipment and adopt new printing practices. Water-based inks required increased drying capacity, they could only be used on certain materials and not on metals or plastics, water-based inks would dry on the printing equipment such as the rollers or screens causing them to be ruined, they had poor print quality, poor blocking resistance, poor water resistance, poor abrasion resistance, and a number of other disadvantages. Through the addition of additives like high molecular weight resins, waxes, surfactants, and other materials the physical properties of water-based inks have greatly improved. All though in the past there were many disadvantages to using water-based inks when compared to the other solvent based inks they now offer better performance, lower printing costs, and are a less damaging alternative to both people and the environment.

Applications:

Due to the major advances in water-based ink technology over the last forty years water-based inks can now be readily applied to most materials even plastics and foils, through the use of surface preparation techniques like the corona treatment. Through the development of new additives and printing processes water-based inks can now be used in the majority of printing process and on most materials and for many different applications. Water-based inks excel in printing applications involving paper, cardboard, and textiles, are even used to print on foils, plastics, and food packaging. One of the major applications for water-based inks has come about in the last decade, the ink-jet printer. As the number of personal computers increased so did the demand for printers and thus the ink. The water-based inks used in many ink-jet printers function in a similar way to other water-based inks in terms of the application of the ink to the substrate or surface. The ink is brought into contact with the surface, there is a delay in wetting and evaporation starts, wetting and penetration into the substrate or surface occurs while the solvent continues to evaporate until it is dry, see figure 10. Figure 11 shows a SEM photograph of a ink droplet from a ink-jet printer on the surface or the substrate, while figure 12 shows the ink droplet after it has wetted and penetrated the substrate or surface and the solvent has evaporated.[4]

Manufacturing of Water-Based Ink:

The manufacturing of water-based inks is a simple mixing process. The pigments, additives, and vehicle are each produced separately. When pigments are produced they are typically of a size that is too large to be used in inks. The pigments are ground or milled to particles sizes between 5µm to 10nm depending on what color strength, coating thickness, and dispersion properties are wanted. The pigment is then mixed in a high speed mixer with the solvent or solvents which in the case of water-based inks is going to be either mostly water or all water. The surfactant and/or polymer are added to mixer to stabilize the colloidal dispersion and allow for even distribution of the pigment. The additives are then added to the mixer to achieve the desired properties, which completes the ink making it ready for use.[3]

Formulations of Water-Based Ink:

Inks are made up of colorant, vehicle, solvent, and additives. There is what seems to be an infinite number of water-based inks. There are thousands of different pigments, additives, and vehicles that are used in different combinations and amounts to achieve the desired properties of the ink. For water-based printing inks, they typically will have a composition of 60% water/other solvents, 20% vehicle (resin), 15% colorant, and 5% additives. A more detailed breakdown can be seen in figure 8. A typical water-based ink composition for ink-jet printers can be seen in figure 9. The composition of a water-based ink used in flexographic printing on paper can be seen in figure 13.

Conclusions:

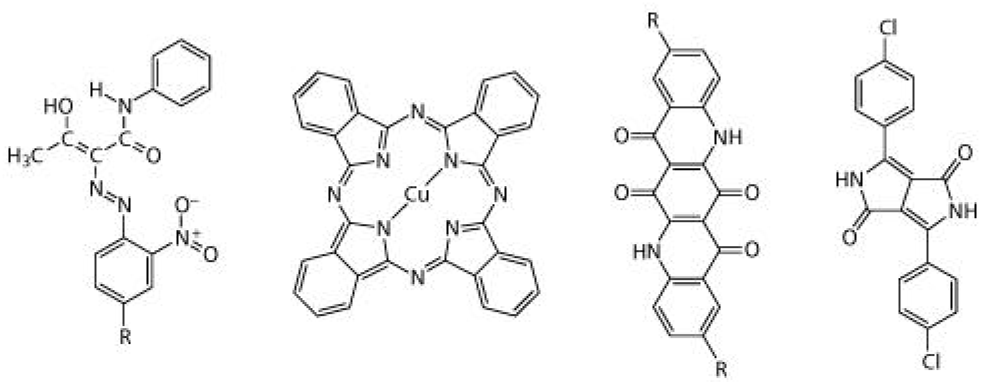
Over the last forty years significant developments have been made with water-based ink technology. All though research has slowed over the last several years advancements in water-based ink technology will continue for some time. Currently there is no viable alternative to water-based inks when environmental and health concerns are taken into account. In time the use of inks will decrease as more material that was printed in the past becomes electronic, such as with the trend of books being available electronically, letters being replaced with email.

Figure 1

Sales of various inks in the US* ($m)	
Offset	2200
Flexo	1100
Gravure	600
UV/EB	300
Screen	250
Letterpress	100
Inkjet	~300
Total sales in the US:	***ca*** **4700**

* Total sales worldwide are estimated to be $13,500m (*ca* ££9000m). The breakdown is expected to follow the same trend as above. *Source: David Savastano,* Ink World, *2001*

Figure 2



(1) Azo pigment (2) Copper phthalocyanine blue (3) A typical quinacridone (4) Diaryl pyrrolopyrrole

(Source: http://www.chemsoc.org/chembytes/ezine/2003/kunjappu_mar03.htm)

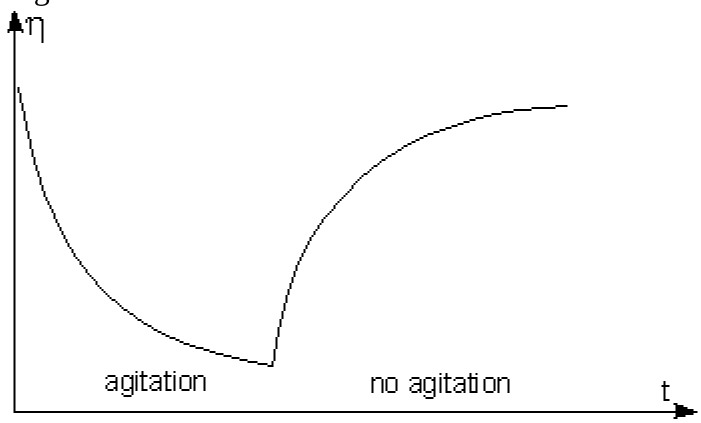
Figure 3

Process	Binder	Solvent
newsprint	hydrocarbon resins, e.g. asphalt	mineral oil
offset	drying oils alkyd resins modified rosin hydrocarbon resins	mineral oil

metal decorating	alkyd resins melamine resins	mineral oil
publication gravure	modified rosin hydrocarbon resins	toluene
flexo, packaging gravure	nitrated cellulose polyvinyl acetate polyamide resins	alcohols esters ketones mineral spirits
water based flexo, packaging gravure	maleic resins acrylic resins shellac	water alcohols

(Source: http://www.hdm-stuttgart.de/projekte/printing-inks/p_gercom.htm)

Figure 4



(Source: http://www.hdm-stuttgart.de/projekte/printing-inks/p_gercom.htm)

Figure 5

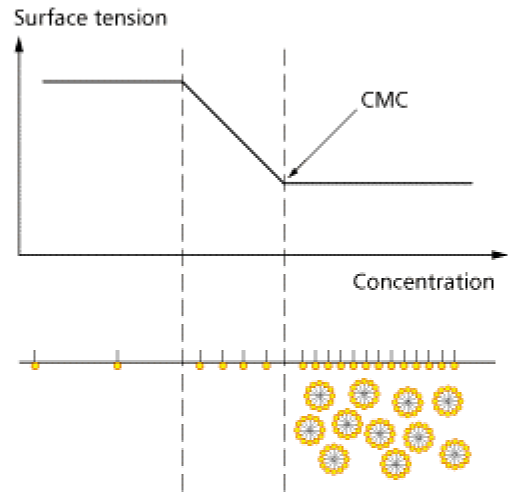
General Comparison of Different Chemical Types of Surfactants in Waterborne Systems

Surfactant	Static Surface Tension Reduction	Spreading Ability	Dynamic Surface Tension Reduction	Foaming
High-molecular-weight silicone surfactant	+	-	O	O
Low-molecular-weight silicone surfactant	++	++	+	+
Non-ionic fluoropolymer surfactant	+++	O	-	-
Organic surfactant	+	O	+++	+++

+++ outstanding, ++ very good, + good, o acceptable, - poor

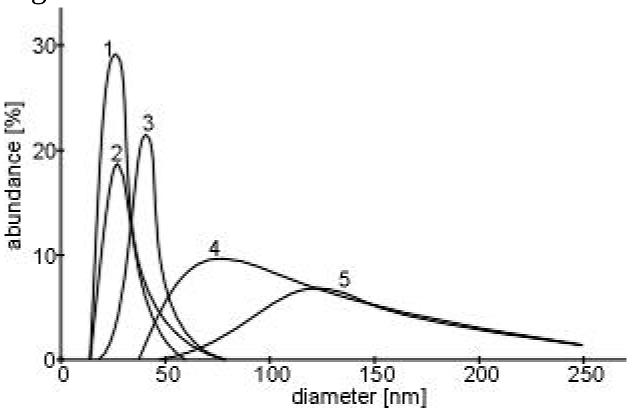
(Souce: Heilen)

Figure 6



(Source: http://www.chemsoc.org/chembytes/ezine/2003/kunjappu_mar03.htm)

Figure 7



1	Channel Black,	surface about	110 m²/g
2	Furnace Black,	surface about	80 m²/g
3	Acetylene Black,	surface about	65 m²/g
4	Lamp Black	surface about	20 m²/g
5	Blacking	surface about	15 m²/g

(Source: http://www.hdm-stuttgart.de/projekte/printing-inks/p_gercom.htm)

Figure 8

Component Paper Printing Film Printing		
Organic pigment	12 to 15	12 to 15
Resin	10 to 25	15 to 25
Alcohol	0	2 to 5

Additives (waxes, antifoamers, dispersing and wetting agents, microbiocides)	5 to 7	6 to 10
Water	53 to 73	45 to 65

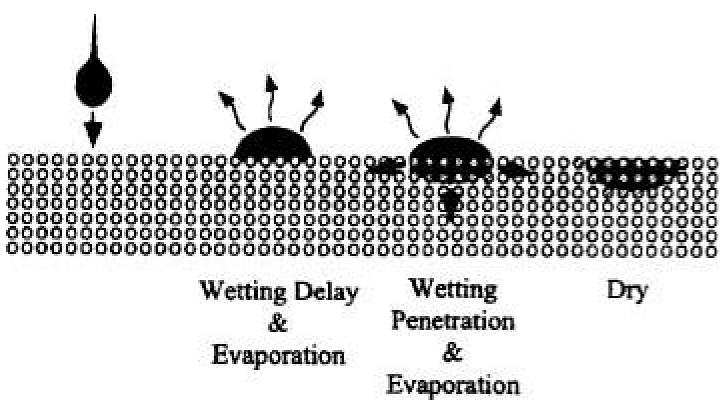
(Source: Ullmann)

Figure 9

Component	Function	Concentration, %
Deionized water	Aqueous carrier medium	60 - 90
Water soluble solvent	Humectant, viscosity control	5 - 30
Dye or pigment	Provides color	1 - 10
Surfactant	Wetting, penetrating	0.1 - 10
Biocide	Prevents biological growth	0.05 - 1
Buffer	Controls the pH of ink	0.1 - 0.5
Other additives	Chelating agent, defoamer, solublizer etc.	> 1

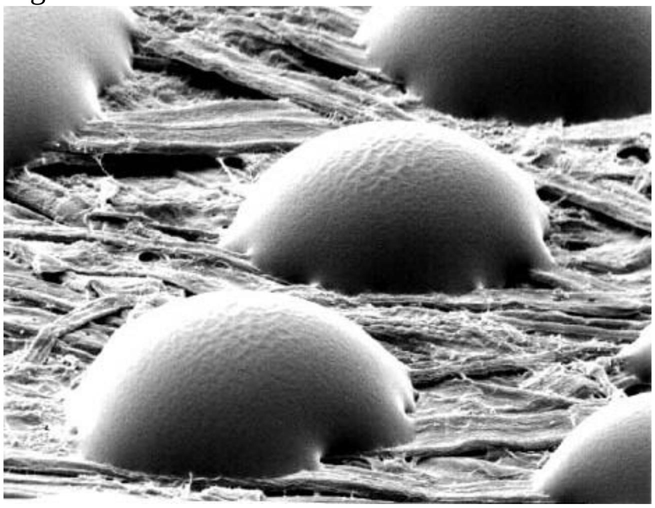
(Source: http://www.imaging.org/resources/leinkjet/part4.cfm)

Figure 10



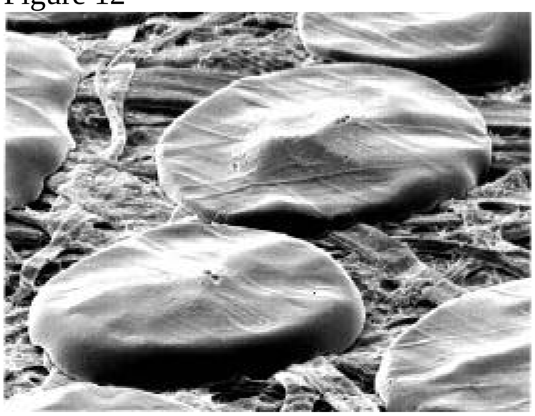
(Source: http://www.imaging.org/resources/leinkjet/part4.cfm)

Figure 11



(Source: http://www.imaging.org/resources/leinkjet/part4.cfm)

Figure 12



(Source: http://www.imaging.org/resources/leinkjet/part4.cfm)

Figure 13

CI P. Red 49	18.0
Acrylic/alkali water varnish	60.0
Polyethylene wax	4.0
Isopropyl alcohol	4.0
Water	13.9
Silicone anti-foam	0.1
	100.0

(Source: http://www.hdm-stuttgart.de/projekte/printing-inks/p_gercom.htm)

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