Water-based inks for packaging films

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The use of water-based inks on nonporous packaging film and foils presents a challenge to the ink formulator.

In today's changing market, the use of films and laminations has increased dramatically. Environmental constraints have forced ink makers into using new methods of formulating acceptable inks. One of the largest growth areas—and, unfortunately, the most difficult formulating challenge—has been in the use of water-based inks on films and foils. Prints on porous substrate such as paper or board were one of the first successful uses of water-based inks. The forgiving nature of paper and board allowed wide formulating latitude. The single property that made paper so easy to print on was its absorbent nature. The obvious differences between drying solvent and water-based inks were reduced, since the substrate could be counted on to absorb a significant amount of water. Wetting was also less of a factor, since the substrate allowed water to be easily "wicked up."

As the use of water-based inks grew, so did the types of substrates. Film and foil printers demanded water-based inks for their needs. The formulator could no longer depend on any help from the substrate. The various nonporous substrates would not allow any drying by penetration, adhesion was poor, and poor printability was the rule. Nevertheless, the challenges of water-based inks are being met using today's technology.

Typical composition of water-based inks

A typical water-based ink contains pigment, binder (resin), water, additives (surfactants, waxes), and solvents. **Table I** shows the typical percentages of these components.

Pigments are normally incorporated into an ink formulation by using a concentrated base. A "base" or pigment dispersion can contain anywhere from 40-60% pigment (depending on type). Water systems use the typical dispersion methods found in most ink plants but have a unique advantage over solvent systems. In solvent systems, a great deal of technology is used to remove the pigment from the aqueous nature of the "strike" tank. Unfortunately, the act of drying and concentrating the pigment particles usually causes agglomeration to occur. Water-based systems, however, can use the pigment as presscake before it is dried. Some presscakes today can have as little as 50% water and are referred to as high solids presscakes. The water in the presscake can be easily incorporated into the final ink formulation, and the dispersion process can be made much easier. Unfortunately, the evaluation of the dispersions has become critical and can consume a great deal of testing.

I. Typical water-based ink composition

Pigment	10-45%
Binder (resin)	10-25%
Water	40-75%
Solvent	0-20%
Additives	1-7%

Printing on foil and film has added a new dimension to those old paper inks that were so successful. Now transparency, gloss, and stability are critical. The venerable grind gauge so often used to evaluate solvent inks is now sadly inadequate. The microscope, with various upgrades, has begun to see more use. Dispersions are now judged for acceptability by image analyzers. The resulting pigment bases are now able to be controlled by acceptable particle size rather than by "scratches" on a metal surface.

With the new technology, new problems have surfaced. Inks with smaller particles are not more stable or transparent. On occasion, pigments will "kick out," and flocculation seems to occur spontaneously. The culprit has been found to be the electrical charge of the pigments in the inks or bases.

Zeta potential, common in other industries and research labs, has begun to see more use. The zeta potential, or charge of the pigments, can be easily affected by the addition of certain surfactant packages. Conflicting charges will cause flocculation, increased opacity, and poor stability. Formulations that fail to consider the "potential" of the system can cause many problems that seem unexplainable. The ink formulator now has to consider factors that were previously ignored.

The latest of these factors is VOCs (Volatile Organic Compounds). Environmental considerations have caused the formulator to need to know how much VOC is present in a dispersion as well as its chemical nature. A new set of specifications for pigment dispersions is presented in **Table II.**

Current binders or resins basically come in three forms: water soluble, water dispersible, and emulsions. Water-

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II. Typical dispersion specifications

	Old	New
Fineness/grind	O-O grind gauge	$< 1 \mu m$
Zeta potential	none	+, -
pH	Documented	Documented
Amine content	Documented	Documented
VOCs	Not reported	Percentage/type

III. Expansion of a typical water-based ink formulation

Presscake 50% water (organic)	20-50%
or	
Pigment (inorganic, dry)	40-60%
Solution resin (30% NV)	5-10%
Additive (amine)	0.5-1%
Emulsion resin (50% NV)	30-50%
Water	5-10%
Solvent	0-20%
Additives	1-7%

soluble resins are usually styrenated acrylics, styrene maleic anhydrides (SMA), or rosin-modified resins. The styrenated acrylics are the most common. They are neutralized with an amine to produce a solution in water. These resins are commonly found in the pigment dispersions previously mentioned. Styrenated acrylics often have good pigment wetting properties and impart improved printability. They "rewet" easily and prevent "drying-in" of cylinders and plates. Unfortunately, they have poor chemical resistance, especially against amines.

Emulsions are high molecular weight polymers that are supplied as emulsions in water. Usually low in viscosity, they are used to improve chemical resistance, improve dry speed, increase adhesion, and increase solids. They "rewet" poorly and do not wet pigment very well. Water-dispersible resins usually have smaller resin particles than the emulsions. They have properties between those of emulsions and solution-type polymers. The typical formulation found in Table I can now be expanded to the formulation in **Table III.**

The film-forming nature of water-based polymers is much different from traditional resins employed in solvent inks. The amine that is used to neutralize the acidic solution-type resins forms a salt that is water soluble. As drying occurs, the amines are released, and the solution resins form a film. This film is easily redissolved using amine-containing water. As previously mentioned, this is the mechanism behind solution-type resins having good "rewet" properties and poor chemical resistance.

Emulsion-type polymers, however, do not form a film on their own. They need to coalesce into a film. A combination of heat, additives, and solvent enable the resin particles to unite to form a continuous film. As a general rule, the glass transition temperature (Tg) of the resin is a good indication of how readily the emulsion will form a film. Low-Tg emulsions are the most common type used in water-based inks for film. Solvents and additives that have an effect on the emulsion "particles" also can speed up film forming. Once the film is coalesced, it will not resolubilize— thus the emulsion polymers' superior chemical resistance and poor "rewet" characteristics.

Surface energy and surface tension

Water will "bead up" on the surface of a foil or film. The reason for this phenomenon is the existence of surface tension. The subject is much too broad and diverse to do justice here, but a brief explanation will help explain the

IV. Typical nonporous substrates

Chemical nature	Type
Cellophane	Nitrocellulose coated
	PVDC coated
	Uncoated
Nylon	Uncoated
	PVDC coated
	Metallized
Polyester	Uncoated
	Treated
	PVDC coated
	Metallized
Polyethylene	Linear Low Density
	Low Density
	Medium Density
	High Density
Polypropylene	EVA modified
	Non-oriented
	Oriented
	Oriented metallized
	Acrylic coated
	PVDC coated
Foil	Uncoated
	Shellac coated
	Nitrocellulose coated
	Vinyl coated

V. Typical water-based ink for film and foil

Pigment base	
Presscake 50% water (organic)	20-50%
or	
Pigment (inorganic, dry)	40-60%
Solution resin (30% NV)	5-10%
Amine	0.5-1%
Antifoam	0.2-0.5%
Surfactant	0.1-0.5%
Letdown	
Emulsion resin (50% NV)	30-50%
Water	5-10%
Solvent (alcohol)	0-20%
Antifoam	0.2-0.5%
Wax	0.5-1.0%
Fungicide	0.0-0.1%
Amine	0.5%
Surfactant(s)	0.5-1.0%

concern with which surfactants are added to ink formulations.

A simple explanation of surface tension is that force which results from unbalanced molecular attractions that occur at the surface of liquids. It is expressed as force per unit length or dynes per centimeter. If we substitute solids for liquids in the above area, we have the definition for surface energy often expressed as ergs/cm^2. It is important to note that both surface tension (expressed as dynes/cm) and surface energy (expressed as ergs/cm^2) are numerically equal. It is common practice to use surface tension when describing liquids and surface energy when describing solids.

The previous definition can now be expanded to include two separate forces, dispersion and specific, that together make up the total surface energy. Bassimer and Krishnan* describe surface energy as the combination of two forces, dispersion and specific. Specific forces can arise from dipole or polar attractions, acid-based reactions, and hydrogen bonding reactions, as well as other causes. Specific forces are often lumped together and known as "polar" forces.

Wetting occurs when the surface tension of the liquid is lower than the surface energy of the substrate. Conversely, if the surface tension of the liquid is higher than the surface energy of the substrate, no wetting occurs. The familiar "beading up" of water on polyethylene film, for example, is caused by the high surface tension of water (72 dynes/cm) and the relatively low surface energy of polyethylene (31 ergs/cm^2). Solvent inks rarely encounter this problem with surface tensions in the range of 20-25 dynes/cm. They are able to "wet" the surface of many polymers without difficulty.

Adhesion is also governed to a large extent by surface energy interactions. The surface energy of the wet ink film should be equal to or lower than the surface energy of the substrate to get good adhesion. The explanation has been expanded to include that not only must the total surface energies of the wet ink film be equal or less than the substrate, but their polar components should be as close as possible as well.

Practical measurements and application of surface energy

As water ink applications grew for films and foils, the ink formulator began to use instruments to measure surface energies and tensions. The Goniometer was revisited and provided much needed basic information on the wetting of films, foils, and inks. The DuNouy Tensiometer was also used to measure surface tensions of the liquid inks. Both instruments were time-consuming to use, difficult to clean, and, probably most significantly, provided only static measurements. Since the interaction of inks, plates, rollers, and substrate could hardly be described as a static environment, new instrumentation was developed to measure surface energies dynamically.

Today most liquid inks can be evaluated for surface tension dynamically with a maximum bubble pressure type of instrument. The Sensadyne 6000 by Chem Dyne Research Corp. is typical. The instrument in operation bubbles gas through a medium (i.e., ink) and calculates the surface tension at various bubble rates. These bubble rates can be related to press speeds. Substrates and ink can be measured dynamically using a method in which a substrate is "dipped" in a "probe" (known) solution at a controlled rate, using an instrument which measures buoyant force. The data are then analyzed and the surface energy, including both the dispersion and specific forces, is obtained. A instrument typical of this type is the Cahn DCA 312 from Cahn Instruments Inc.

Substrate

Table IV lists some common nonporous substrates. It is not meant to be all-encompassing but to demonstrate the wide variety of substrates that water inks have been printed on. Surface energies vary between the substrate and among similar types, depending on the manufacturer. Film manufacturers and printers have been educated in the use of corona treaters that help to raise surface energy levels to a workable level (>35 ergs/cm^2) by using electrical discharge. These units not only increase the surface energy but roughen the surface. Scanning electron microscopes have proven useful in characterizing the surface of treated films and foils and investigating lamination structures.

Modifying water-based inks for films

By far the most significant additive in water inks for packaging films is the surfactant packages. Armed with information and characteristics about the surface energy of the substrate and the final application, the ink formulator must decide on the best surfactant or combination of surfactants to use. Sometimes the choices seem endless, as combinations of surfactants can behave quite differently from their individual components. Not only must the surfactant lower the surface tension of the ink, it also must not create incompatibilities within the resin system or dispersion. When added to an ink, the wrong surfactant can cause "kick-out" and flocculation almost immediately. The surfactant must not cause an undue amount of foaming, because correcting the situation by using an antifoam may render the surfactant useless. The final ink application must also be considered, for a surfactant that reduces or limits chemical resistance properties (i.e., grease resistance or alkali resistance) is not practical. Stability of the surfactant is also important, as some materials can lose their ability to reduce surface tension, depending on the ink system.

Solvents provide another useful purpose besides improving dry speed and accelerating the film-forming capability of emulsion resins. Alcohols are the most common solvents found in water-based ink systems. Currently, the maximum usage permitted for inks to be compliant is 25% by volume of volatiles. Since alcohols have a surface tension of approximately 22 dynes/cm, they can reduce the overall surface tension of the ink system quite significantly.

The addition of solvents, however, is not without problems. Since they are by nature volatile, the formulator must be sure to balance the properties of the entire ink system when choosing a solvent. For example, it would

*Bassimer, R., and Krishnan, R., 1990 Flexographic Technical Association Proceedings, Ronkonkoma, N.Y., p. 7, "Practical Applications of Surface Energy Measurements in Flexography," March 1990.

be foolish to use a fast-drying alcohol to increase dry speed, ignoring the fact that the surface tension would rise as the alcohol evaporated. A fast-drying ink with poor printability would most likely enjoy a very limited market. On the other hand, alcohols, when chosen wisely, can reduce the amount of surfactant needed, increase dry speed, reduce foaming, and reduce the heat requirement needed for emulsion resins to coalesce.

Antifoams and additives

Despite careful selection of surfactants and low-foaming resin systems, and the use of an appropriate alcohol, antifoams are generally needed. As the antifoams reduce foam occurring at the surface of an ink, they also can destroy all the surface properties previously formulated into the system if chosen unwisely. Antifoams must be evaluated for compatibility with the entire ink system before being selected for use. The most common types of antifoams are based on silicone or fatty alcohols/esters. As with surfactant selection, the final application must be considered. Overcompensating for poor formulation by the addition of antifoams invariably leads to "fisheyes," mottle, blocking problems, and flocculation.

The stability of the antifoam is also of primary importance. Since some antifoams by their nature congregate near the surface of an ink, how do they behave under constant agitation, as in a press? Many an unfortunate formulator has found that his carefully selected antifoam "disappears" when in an ink sump for extended press runs.

Additives that do not fall into any of the previously mentioned categories are generally related to the end use of the printed product and are not needed in the actual printing process. Waxes, silicones, biocides, and fungicides fall into this category. Waxes and silicone provide the same function that they do in solvent inks—improving scratch and mar resistance. Biocides and fungicides allow long-term storage of inks without the formation of pump-clogging and odor-causing plant life.

Typical water-based inks for film and foil

Table V shows the increasing complexity of the water-based ink formulation. A small amount of an amine is added in the letdown portion of the ink to adjust pH to the required level. As previously mentioned, amines are necessary to solubilize the solution-type resins, but they are also used to improve rewetting and stability. Amines can either be slow- or fast-drying and, depending on their structure, may contribute to the final properties of the ink.

Conclusion

Water inks for use on packaging film and foils present quite a challenge to the ink formulator. Increased chemical knowledge and experience in surface science will produce better ink formulations. Dedication and assistance from experts in various fields, from plastic engineers to surface scientists, will enable ink companies to provide solutions to future packaging needs.□

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