No. 08-12

DATE: December 23, 2008

TO: Company Representatives – Members and TAM’s

FROM: George Fuchs & John Daugherty

Formulating Printing Inks to Minimize Environmental Impact©

Summary
This document addresses printing ink compositional factors that have the potential to help minimize their impact on the environment. This includes the use of bio-derived renewable raw materials, the amount of volatile organic compounds (VOCs), presence of hazardous air pollutants (HAPs), heavy metal content, and toxic/carcinogenic ingredients. In addition, printing ink manufacturers must take these environmental factors into account, while also providing a product that meets both the performance expectations on the printing press and the end use requirements of the printed product.

Introduction
At present, there is no regulatory or industry consensus that defines how to minimize the environmental impact of manufactured products. The USDA defines “environmentally preferable” to mean "products that have a lesser or reduced effect on human health and environment when compared with competing products that serve the same purpose”. In the commercial context, it is generally accepted to mean the formulation of products with chemicals and other materials that have a relatively minimal adverse impact on the environment through the manufacture, use and disposal/recycling of the product. Printing inks as formulated chemical mixtures, have quantifiable properties that can be used to make technically sound assessments of environmental impact. Please note that the term “environmentally friendly” is not well defined and cannot be meaningful applied to most industrial products.

The two most basic controlling factors for printing ink formulations are: 1) Physical form (liquid, paste or solid) required to use on the designated printing equipment 2) Drying methodology.

Both of these parameters vary widely among the different printing processes and can be limiting factors in any of the formulation techniques that are used to reduce environmental impact.

The physical form is governed by the printing press and its ink application system. For example paste inks are required for the lithographic offset system to distribute evenly on multiple rollers and then onto the plate and blanket. Gravure and flexographic inks must
be very fluid to transfer from the ink reservoir to the more simplified ink distribution system and onto the substrate. All printing inks (with the exception of solid inks) go through a conversion from a wet phase to a dry durable film by a variety of physical and/or chemical processes that include oxidation, evaporation, substrate absorption or exposure to an ultraviolet light/electron beam source. Each type of ink has limitations in terms of the level of volatile content and ability to utilize renewable raw materials. Table 1 shows the key differences among the various printing processes.

**TABLE 1**

<table>
<thead>
<tr>
<th>INK TYPE</th>
<th>INK CHEMISTRY</th>
<th>DRYING PROCESS*</th>
<th>VOC COMPOSITION</th>
<th>TYPICAL % VOC</th>
<th>ON PRESS EMISSION CONTROLS</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>PASTE INKS</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Offset Sheetfed</td>
<td>Oleo resinous</td>
<td>Oxidation</td>
<td>Aliphatic hydrocarbons</td>
<td>0-20</td>
<td>None</td>
</tr>
<tr>
<td>Offset Heatset</td>
<td>Oleo resinous</td>
<td>Evaporation</td>
<td>Aliphatic hydrocarbons</td>
<td>35-45</td>
<td>Afterburners</td>
</tr>
<tr>
<td>Offset Coldset</td>
<td>Oleo resinous</td>
<td>Substrate absorp.</td>
<td>Aliphatic hydrocarbons</td>
<td>2-20</td>
<td>None</td>
</tr>
<tr>
<td>Energy Curable</td>
<td>Acrylated monomer/oligomer</td>
<td>Polymerization</td>
<td>Unknown</td>
<td>0-5</td>
<td>Venting to atmosphere</td>
</tr>
<tr>
<td><strong>LIQUID INKS</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Flexo-Gravure</td>
<td>Solvent Various resin-solvent combos</td>
<td>Evaporation</td>
<td>Various solvents</td>
<td>40-70</td>
<td>Afterburners</td>
</tr>
<tr>
<td>Flexo-Gravure</td>
<td>Water Various resin types</td>
<td>Evaporation</td>
<td>Alcohol (if present)</td>
<td>0-2</td>
<td>Venting to atmosphere</td>
</tr>
<tr>
<td>Gravure</td>
<td>Resin-toluene</td>
<td>Evaporation</td>
<td>Toluene</td>
<td>40-70</td>
<td>Recapture</td>
</tr>
<tr>
<td>Inkjet Solvent</td>
<td>Various resin-solvent combos</td>
<td>Evaporation</td>
<td>Various solvents</td>
<td>40-90</td>
<td></td>
</tr>
<tr>
<td>Ink Jet Water</td>
<td>Various resin types</td>
<td>Evaporation</td>
<td>Water</td>
<td>0-5</td>
<td>None</td>
</tr>
<tr>
<td><strong>SOLID INKS</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dry Toner</td>
<td>Various thermoplastic resins</td>
<td>Fusion via high heat</td>
<td>None</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>Hot Melt</td>
<td>Resin &amp; wax</td>
<td>Melt &amp; resolidify</td>
<td>None</td>
<td>NA</td>
<td>NA</td>
</tr>
</tbody>
</table>

* All printing inks also dry by absorption into the substrate, dependent on the porosity of the substrate
Listed below are some of the key formulation tools that can be utilized to lessen the environmental impact of printing inks.

- Use of bio-derived renewable raw materials
- Minimizing or reducing the level of volatile organic compounds (VOCs)
- Minimizing, reducing or elimination of hazardous air pollutants (HAPs)
- Eliminating raw materials which contain toxic heavy metals
- Eliminating materials that are classified as toxic or known carcinogens
- Ensuring that ink waste can be classified as non-hazardous
- Ensuring the dry ink does not impede any potential recycling or does not present a hazard when going to a landfill.

Bio-derived Renewable Raw Materials
For the purpose of this report, bio-derived renewable materials are defined as any material originating from plants, animals or naturally derived sources (such as water) that can be replenished in the short term. Soy oil is often mentioned as a renewable material, but represents only one option in this regard. There are well over sixty types of bio-derived renewable materials that can be used in printing inks.

The use of bio-derived renewable materials in place of petroleum sourced materials is a measurable property and is generally believed to improve ink’s overall environmental profile. Examples are:

- Oils from plants and trees such as flaxseed (linseed), chinawood (tung), soy, corn, safflower, etc. (also referred to as vegetable oils).
- Materials based on animal sources such as fish oil, tallow, some colorants
- Materials based on insects such as shellac, some specialized colorants
- Resins based on plant or tree sources such as wood rosin, tall oil rosin, gum rosin, nitrocellulose
- Plant derived solvents such as ethyl lactate, grain derived alcohols
- Fatty acid esters such as tall oil fatty acid methyl ester
- Naturally renewed resources such as water

It is important to note that gauging the full environmental impact resulting from the use of these materials is highly complex and somewhat subjective, requiring certain assumptions and arbitrary determinations as to how far back one goes into the overall process. Minimally, this would include a comprehensive evaluation of the manufacturing process and refinement for use of the bio-derived renewable materials. The initial stages include aspects such as planting, fertilizing and harvesting, followed by the refining stage that includes air emissions, energy usage, water discharges, by-products, and generated wastes. For example, plant derived materials start from the time the seeds are planted in the soil to delivery of the product to the ink manufacturer.

There have been very few life cycle studies conducted on materials used by the ink industry due to the complexities, cost and time involved. Battelle* conducted a life cycle
study in 1998 of soy based sheetfed ink, but did not draw any clear cut final conclusions regarding the environmental impact of soy versus petroleum oils.

*Streamlined LCA of Soy-Base Ink Printing conducted by Life Cycle Management Group of Battelle, July 1998

VOC Content
Reducing product VOC content is a generally accepted technique for reducing environmental impact because lower VOC containing products emit fewer emissions during manufacture and use. Over the last two decades, ink companies have made a significant effort and investment in developing and reformulating ink systems that have lower VOCs than inks sold previously for similar applications while continuing to meet customer requirements.

The percentage of VOC in an ink is highly dependent on the type of ink, with some inks requiring a higher level of VOC in order to function and dry during the printing process. For example, a heatset ink that dries by evaporation will contain a higher concentration of VOCs than a sheetfed ink that dries by oxidation. Water based inks will generally have lower VOC content than solvent based products. See Table 1.

It is important to note that many printers employ sophisticated “capture and control” mechanisms to minimize air emissions during the printing process. Typical examples are publication gravure inks (largely based on toluene), where the solvent recovery systems used on the printing press are near 99.5% effective. The “recovered” solvent is reclaimed and recycled to make more ink or for other uses. Heatset printers using aliphatic hydrocarbon based inks, typically employ catalytic afterburners to eliminate or minimize VOC emissions from the process, as it is not possible to recapture these types of materials. In addition, a certain amount of the VOC in a printing ink is retained in the substrate. Most, but not all regulatory jurisdictions accept a 95% retention factor for coldset and sheetfed/oxidizable inks and 20% retention for heatset inks. Energy curable inks (ultraviolet and electron beam) are another approach, as the amount of VOC is minimal upon polymerization.

Hazardous Air Pollutant Content
Hazardous air pollutants (HAPs) are those materials that are known or suspected to cause cancer or have serious health effects, such as reproductive effects or birth defects, or adverse environmental effects. EPA has identified 188 specific chemicals as HAPs, which are listed in Section 112 of the Clean Air Act. HAPs can also be volatile organic compounds (VOCs) depending on the physical/chemical properties of a particular material. Similar to VOCs, lowering the amount of HAPs contained in printing inks is another way of reducing the overall environmental impact. Among other requirements, The Printing and Publishing MACT standard specifies a compliant ink as one that contains no more than 0.04 weight fraction organic HAP. Some gravure and flexographic inks are based on high levels of solvents classified as HAPs and rely on recapture techniques to minimize emissions of such products.
Heavy Metals
Essentially, all inks sold in the U.S. today are manufactured without the use of compounds based on toxic heavy metals (i.e. lead, arsenic, selenium, mercury, cadmium and hexavalent chromium).

Federal health and environmental regulations were enacted in the United States beginning in the 1970's that made the usage of the known highly toxic metals as printing ink formulation components an unattractive option and ultimately resulted in the large-scale removal of these metals from commercial usage in printing inks. For further information, see NPIRI Bulletin 08-05, Metals in Printing Inks.

Absence of Toxic or Carcinogenic Chemicals
Ink manufacturers, for the most part, use materials that are classified as nontoxic and noncarcinogenic according to the OSHA hazardous classification. Exceptions must be listed on the product Material Safety Data Sheet (MSDS).

Recycling of Printed Products
Most inks can be de-inked from printed paper so that the paper can be recycled to create fiber used to make more paper. When inks are printed on other substrates such as plastic films, rigid plastics, glass or metal, other recycling methods need to be utilized.

Regulatory Classification of Waste Ink
Hazardous waste is defined by the EPA under the Resource Conservation & Recovery Act (RCRA) regulations. Non-solvent waste ink that has not been contaminated with other pressroom materials is not considered a hazardous waste. Any ink waste containing solvents with a flash point of less than 100 degrees F would be classified as hazardous due to flammability. De-inking sludge from the recycling of printed materials would have the same classification.

Biodegradability Status
A product is deemed biodegradable if it is capable of undergoing biological anaerobic or aerobic decomposition into carbon dioxide, methane, water, and inorganic compounds, or biomass in which the predominant mechanism is the enzymatic reaction of microorganisms and is completed in a relatively short period of time.

U.S. FTC CFR 16 Part 260, “Guides for the Use of Environmental Marketing Claims” states that claims of degradability, biodegradability or photodegradability should be qualified to the extent necessary to avoid consumer deception about: (1) the product or package’s ability to degrade in the environment where it is customarily disposed; and (2) the rate and extent of degradation.” Further, the degradable, biodegradable or photodegradable status must be substantiated by competent and reliable scientific evidence that the entire product or package will completely break down and return to nature, i.e., decompose into elements found in nature within a reasonably short period of time after customary disposal.

It is important to recognize that these biodegradability definitions would exclude the vast majority of commercially available chemicals. While there are individual printing ink
components that meet the definitions, generally the mixture as a whole would not qualify as biodegradable.

The ink industry position on biodegradability is as follows:

- It is important to recycle printed materials. Landfill disposal or incineration is an unnecessary waste of precious resources.
- When printed products are discarded in a landfill, it must be noted that they consist of a very small quantity of ink in relation to the much larger amount of substrate, and therefore the overall biodegradability is heavily dependent on the degradation of the substrate.

Other Factors
There are factors other than ink composition that play a role in environmental impact. This would include sustainability based on life cycle analysis of the materials, ink manufacturing and the printing process. These will be addressed in future reports.