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To help us learn more about the most environmentally responsible print methods we enlisted our our friends at Brown and Williams Environmental LLC (http://bw-environmental.com/) and asked them to survey the existing ink technologies on the market. Here is what they came back with:

Environmental Attributes and Issues with Printing Methods

As much as we strive to reduce the impacts of our printing, the fact is that there is no environmentally perfect printing system. But for any given printing scenario there are better and best choices. In general these choices strive for fewer toxic ink and process related compounds, fewer solvents, and less processing in general. There are tradeoffs – get rid of one bad chemical and you may need more water for cleanup – or energy for curing. Remove PVC from the plastisol formulation and ink costs might go up. It is all an environmental balancing act. To make matters even more complicated design, application, durability and price all end up in the balancing act!

But at econscious we have developed several "rules of thumb" to assist our process of selection the best printing systems and materials for the specific product at hand. In general, our hierarchy is as follows:

The best printing choice (if applicable) is water-based inkjet printing with non-toxic or least toxic inks and processing aids.

For discharge printing, we prefer the non-formaldehyde based systems

For traditional plastisol printing, better means lower solvent content (VOCs) and heavy metal free. Best is solvent free, phalate free, heavy metal free – and best of the best is PVC free if obtainable.

It is important to know that no matter what printing systems or systems you are considering (waster based, solvent based, plastisol, etc) the composition of inks varies widely. Some inks contain chemicals that would be classified as hazardous. Inks frequently get their color from the metals or hazardous pigments they contain. Inks containing metals and/or those inks using a solvent carrier are often classified as hazardous. It is the responsibility of those working with them to determine whether the inks used in their operations are hazardous. For assistance in making this determination, review the product MSDS.

Most inks may be recycled: spent inks of different colors are often blended to make black ink. For smaller print shops, consider coordinating with larger plants or newspapers (ones that use

rubber or oil based ink) to recycle ink. These businesses usually recycle their inks on-site or ship them off-site in bulk shipments. Also consider purchasing inks from a distributor who will take or buy back unused or spent inks.

PLASTISOL PRINTING (PVC)

PVC Environmental Life Cycle Issues

The most widely used processes in apparel screen printing is probably solvent based plastisol. Plastisol printing inks are typically based on the PVC polymer. So just what is PVC? PVC is the acronym for polyvinyl chloride, a tough, durable, low cost plastic that is the second most popular plastic (by volume) next to polyethylene. PVC has tens of thousands of consumer and commercial uses. It is found in vinyl siding, water based emulsion paints, pipe, wire coatings, and floor tile. Plastisized (softened) versions are used for vinyl fabrics, medical products, plastic wrapping and flexible coatings. Packaging applications include meat wrap, "blister packs" and bottles for edible oils and some non-food products. And many plastisol printing inks.

Pure PVC, with no additives or contaminants, is non-toxic. But you rarely see pure PVC in consumer products. Most of the time, PVC plastic is mixed with various auxiliary chemicals and plasticizers and then the health and safety story is not so rosy.

Unlike most commodity plastics that have only carbon and hydrogen atoms as their main component elements, PVC differs by the addition of chlorine, which increases its compatibility with a wide range of materials and suitability for shaping by a variety of techniques. But the addition of the chlorine also leads to one of the major environmental problems associated with PVC – the formation during its manufacture and disposal of *Dioxins.* PVC manufacture, use and disposal has been identified as the single biggest source of dioxin in the environment. During the PVC environmental life cycle, dioxins are formed during the production of the raw material and if a vinyl product ends up in an incinerator. Dioxins refer collectively to a family of 210 different chemicals including dioxins and furans. As a class, dioxins are among the most toxic chemicals known. Many dioxins are carcinogens and highly potent hormone disrupters. They are harmful to animals and fish, do not easily break down in the environment and, therefore, tend to accumulate. Since they are fat soluble they also tend to bioaccumulation in the food chain. Except for a few laboratory applications, dioxins are never made on purpose, but formed as unwanted wastes and by-products of many reactions involving chlorine, carbon containing molecules and heat.

To make matters worse, one of the basic building blocks for PVC is phosgene gas. Which is notoriously known as a nerve gas used during World War I and was the chemical accidentally released in Bhopal, India in the early 1980's which resulted in the death's of nearly 3,000 people and 100.000 injured in the world's worst industrial disaster.

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Phosgene is used to product the vinyl chloride monomer that is polymerized in polyvinylchloride. In essence, it is what makes up the "links" in the "chain" of PVC. Studies show that vinyl chloride can damage the liver, nerves, and immune system – and that has been found to be a human carcinogen.

Solvents

Most plastisol inks are solvent based. This means that they use one or more of the following chemicals to keep the color part of the ink suspended during the printing operations:

- Hexane
- Methyl-ethyl-keytone (MEK)
- Methanol
- Propylene Oxide
- Xylene
- Methyl-isobutyl-keytone (MIBK)
- Isopropyl Alcohol Ethyl Acetate
- Ethanol
- Propyl Acetate
- Butanol
- 2- Butoxyethanol
- Acetone

Yes, this is a big list. And most of these solvents are considered hazardous air pollutants. Some can help the formation of smog. Most are either acutely or chronically toxic to humans. Several are known or suspected carcinogens, teratogens and mutanogens.

Many printing processes use heat to drive off these solvents. This processes dries or "sets" the ink. This can lead to health and air quality problems if the solvent emitted are not properly taken care of or treated.

Hormone Disruption

PVC is a hard, ridged material. Think of PVC sprinkler pipes. In many instances a chemical must be added to make the PVC soft and pliable. As mentioned previously, common chemicals used to soften PVC are phalates, fatty acids, and alcohols. Of special concern are certain which are known hormone disrupters. These chemicals mimic or interfere with our own delicate hormone system. As a class, phthalates are one of the most prevalent of the hormone disrupting chemicals found in the environment. Hormone disrupting chemicals can lead to a variety of health problems including developmental problems, reproductive problems, increased susceptibility to a verity of cancers, as well as broad implications in lower sperm count in men and fertility difficulties in women.

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Heavy Metals
Many pigments that are used as colorants in printing inks are based on the chemistry of heavy metals. Typical heavy metals include:

- Barium
- Cadmium
- Chromium
- Copper
- Lead Chromate
- Manganese
- Zinc

Like solvents, this is big list and each of these metals has environmental health and safety issues in their lifecycle. Many of these are actually or chronically toxic to humans, can be toxic to wildlife if released to the environment in wastewater and some known human carcinogens.

Better options
The good news is that many companies are facing the challenge of replacing PVC, solvents, phalates and heavy metal containing pigments and inks in their products because of both possible legal restrictions as well as environmental considerations.

Solvent Free Plastisol Inks
Some manufactures are lowering the total volume or solvents in their ink formulations to nearly zero. The good news is that the solvents, and their negative affects, are reduced or eliminated. One possible drawback is that it takes more water to clean processes equipment and screens than solvent based inks. And that the increased water use and the wastes are now going down the drain – to be either treated – or worse, released untreated into the environment.

Phalate Free Inks
Here again, companies have found replacements for dangerous phalates by using other phalates or entirely different, less toxic chemistries. These are preferred.

Heavy Metal Free Plastisol Inks
Some manufactures are producing harmful heavy metal free – or reduced metal content inks. These too are preferred.

PVC Free "Plastisol" Inks
Attention and concern regarding PVC content has motivated some ink manufactures' to find a replacement for PVC for traditional "plastisol" printing applications. These inks are being

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developed primarily around acrylic chemistry. In most cases, this is preferred to anything containing PVC polymers.

WATER-BASED PRINTING

Pros

- No or lower VOCs
- No PVC
- Fewer chemicals/solvents involved in cleanup

Cons

- Can use more energy to power oven/heaters used to evaporate water
- Can still have toxic ingredients and additives

Water-based ink printing systems utilize either dyes or pigments in a suspension with water, where water acts as the primary solvent. But water based does not mean that water is the only is the only solvent, many water base inks contain "co-solvents" which may be petroleum based solvents and contribute to a VOC content of the ink. Evaporation of the water from the ink is required to set or "cure" the ink. Curing is typically assisted with the use of electric or gas operated dryers that require energy and contribute to the emissions of this process. Non-water based solvents are typically added to decrease the time and heat necessary to cure the ink on the fabric. When catalysts or hardeners are added they dramatically reduce the shelf life of the ink.

Nearly all water-based inks, like all other inks, are industrial chemicals. Water-based inks are required to be treated and handled by the same local, regional, and federal laws and regulations pertaining to employee training, storage, handling, and disposal as screen printers as any other kind of textile printing ink. Do not assume that because they are water-based that they can be disposed of simply.

Water-based inks can be cleaned up with water.

Some water-base inks or ink additives may still contain chemicals that are suspected or known to be human carcinogens. Review the Materials safety Data Sheet (MSDS) sheet on any ink and ink systems used to determine if this is the case with any of the inks you use.

Water-based printing systems often contain several auxiliary chemicals that are added to improve the performance of the ink. Compounds are added to assist in textile wetting, thickeners or dispersants might be added to modify flow and defoamers may be added to control foam. These ingredients may or may not be listed in the Hazardous Components section of the MSDS.

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DISCHARGE PRINTING

Pros

- No or lower VOCs
- Non PVC method to print on dark shades
- Fewer chemicals/solvents involved in cleanup
- Thiourea dioxide systems have no/low formaldehyde issues

Cons

- Zinc-formaldehyde-sulfoxylate (ZFS) based chemistry produces formaldehyde (a known human carcinogen) as a by-product
- Can use more energy to power oven/heaters used to evaporate water
- Can still have toxic ingredients and additives
- Some consider it to be the worst of both worlds since the garments must be dyed first and then printed, when in some cases just printing could suffice?

Discharge printing is similar to traditional water-based ink, except that "ink" is actually formulated to remove the original dye from the garment being printed. Discharge printing involves discharging (or removing) the dye in a textile substrate and is often followed by a traditional screen printing of color on the resulting natural (pre-dyed) color of the fabric. These printing systems only work on garments dyed with dyestuffs that are compatible with discharge systems.

However, the oven time for water-based inks — including discharge — is longer than for plastisol inks, slowing production times. Typical oven conditions are one to two minutes at over 300 F.

Discharge requires a heater or dryer that can evaporate all of the water in the time that it takes the textile to pass through the system. Water-based only discharge involves a lot more water to get rid of than the plastisol/water-based combination systems.

Discharge inks require an activator or catalyst to function. The most popular system relies on zinc formaldehyde sulfoxylate (ZFS) as its active ingredient. The newer system uses thiourea dioxide chemistry as its active ingredient.

Discharge ink has a limited pot life once the activator is added- typically one work day. Discharge ink can be "recycled" after once activated as a normal ink on light colored textiles. Waste discharge inks, like all inks in a liquid state, are considered a hazardous waste.

Zinc-formaldehyde-sulfoxylate (ZFS) systems

Zinc formaldehyde sulfoxylate is a reactive chemical commonly used in industrial applications for bleaching. It is also known as Rongalite (registered trademark of BASF), sodium hydroxymethylsulfinate. While its heath effects include irritation of skin, eyes and

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gastrointestinal tract the full toxicological properties of this material have not been fully investigated.
During the heating and curing of discharge inks, formaldehyde and sulfur dioxide gases develop as by-products of the reduction process. Formaldehyde is a known human carcinogen. Proper ventilation of the ovens and/or workplace is crucial. It would be proactive to have any facilities indoor air quality checked for formaldehyde levels.
Waste discharge ink, like all inks in a liquid state, is considered a hazardous waste and must be handled as such. Even though it can not function as a discharge ink after its shelf life, it can be "recycled" by using the ink as a normal ink on light colored textiles.
Garments printed with the ZFS discharge system can have measurable levels of residual formaldehyde that did not off gas from the garment during the curing/heating process. Garments may need to be washed or aired to remove all traces of this chemical. If garments are allowed to sit for a time after printing will outgas much of the residual formaldehyde in a few days, temperature and airflow pending – but consideration of where that formaldehyde is going is of concern if it exposes workers or others, ensure adequate ventilation.
The European Union has a formaldehyde exposure threshold of 75 ppm for apparel for small children and infants. Some EU countries, Japan and other countries law is even more strict – 20ppm for children under 36 months of age. A ZFS discharged garment which has not been laundered or allowed to off-gas could fail these tests.

Thiourea dioxide-activated Discharge Systems
Thiourea dioxide activated discharge inks were developed to avoid the formaldehyde exposure and residues associated with ZFS activated discharge inks. They work in a similar fashion with thiourea dioxide as the chemical reducing agent that destroys the garments original dyestuff.

Synonyms: aminoiminomethanesulphinic acid, thiourea dioxide, formamidinesulfinic acid, formamidinesulphinic acid, as well as several trade names.

Acute health effects of thiourea dioxide include; eye irritation, chemical conjunctivitis, skin and it may cause gastrointestinal irritation with nausea, vomiting and diarrhea. But like ZFS the toxicological properties have not been fully investigated.

It is important to note that thiourea dioxide is a different chemical than thiourea (without the "dioxide"). Thiourea is a chemical known to the State of California to cause cancer.