Reducing VOC Emissions Associated with Ink Jet Marking

Authors: Ms. Ramona Krogman, Marketing Manager, Gem Gravure Co, Inc.
Dr. Rick Elmer, PhD, Director of Research, Gem Gravure Co, Inc.
Mr. Mark Kristoff, National Sales Manager, Gem Gravure Co, Inc.

About the authors:

Ms. Ramona Krogman:
Ms. Krogman started in ink jet technology in 1986 after receiving a BS degree in Chemistry from Benedictine University, Lisle, IL. She began as formulation chemist at Videojet Systems International in Elk Grove Village, IL. During the next 16 years, Ramona served in product support, project management and finally marketing roles. She joined Gem Gravure Co, Inc. in 2003 as Marketing Manager and is currently based in the Hanover, MA headquarters.

Mr. Mark Kristoff:
Mr. Kristoff joined Gem Gravure Co, Inc. in 1994 as Western Regional Sales manager. Having spent the previous 8 years with Formulabs specializing in chemical coatings and inks, Mark brought a wide range of knowledge to the sales group at Gem. Named National Sales Manager in 2004, Mark is currently based in San Diego, CA.

Dr. Rick Elmer:
Dr. Elmer received his undergraduate degree in Chemistry from Evangel University, Springfield, MO and his PhD from Missouri University of Science and Technology, Rolla, MO, in 1992. He serviced at Technical Director at Formulabs for 5 years. After several years as Technical Team Leader at DSM Desotech, Rick joined Gem Gravure Co, Inc. as Director of Chemistry. He is based in the Nixa MO Research Center.

Ink jet printers and inks have provided an economical option for adding identification marks to wire and cable since the 1980's. The ability to print variable data at high speeds without having to contact the surface provides flexibility in wire manufacture and processing. The key to success of the mark comes from the ability of the ink to adhere to the surface, surviving subsequent processing steps. Ink jet fluids can be broken into several main components that contribute to the final characteristics of the printed mark.

Resins provide the backbone of printed drop. The resin binds a color component to the surface of the wire. The chemical nature of the resin determines the strength of the bond. Its drying characteristics affect the amount of time required to 'set' the ink before the wire can be rolled after printing. Chemical compatibility between resin and colorant assures a particulate-free, stable ink.

Pigment/dye provides color to the printed drop. Pigments divide into to two major varieties, inorganic heavy pigment or organic soft pigment.

- Inorganic pigment, the most popular being titanium dioxide, are difficult to suspend in low viscosity ink jet fluids. Pigment particles must remain suspended long enough to survive the shear of the jetting process and be delivered to the surface. To obtain suspension, they are embedded (chipped) in resins. The chemical attraction between resins and carrier solvent of the ink assist with suspension. Additional dispersants are used to boost the suspension.
- Soft pigments are large irregular particles. Although easier to suspend for long period, they lack the opacity of inorganic pigments. Again, suspension is boosted by using a resin in association with the pigment.
- Dyes are used as colorants in many ink jet fluids, but are less successful in wire and cable applications. Dyes are frequently damaged by the high temperatures of wire extrusion applications. In other applications, they leach into the surface of jacket materials, causing the printed code to disappear from the surface over time. Leaching can also be associated with transfer, the creation of mirror image code when hot wire is coiled quickly after processing.

Carrying solvents make up a third building block of jet ink. The solvent used must sufficiently solubilize the resin and colorant. It must allow a component of the ink (added salt or colorant) to disassociate enough to provide conductivity. Dry times are influenced by the vapor pressure of the carrying solvent.

Once the balance of the ink has been established, it must survive the actual process of continuous ink jet. Ink is forced through a fixed orifice similar to a stream of water being forced through a hose. As the ink escapes through the orifice, the opening is vibrated causing the stream to break into droplets after leaving the opening. Charged drops and deflection plates in the printhead of the ink jet unit interact deflecting printed drops into the correct placement to create characters. Unused drops are returned to the ink supply to be recycled into the printing process.[1]

Since the droplets are exposed to air during their flight through the printhead and during the recycling process, they lose solvent to environment through evaporation. A secondary fluid, called make up/solvent, is used within the equipment to replenish the solvent lost. The amount of make up used in an application represents nearly 100% of the solvent introduced to the production environment during operation. Make up/solvent is used to bring the ink inside the printer back into the same balance as the ink provided in the original bottle. Make up composition must not skew the balance of the ink, creating a new mix. This would affect the performance of the ink on the surface and in the printer.

One of the most popular solvents for use in ink jet fluids is methyl ethyl ketone (MEK) $CH_3C(O)CH_2CH_3$. It is commercially available. The chemical is useful in solubilizing gums, resins, cellulose acetates and cellulose nitrate. It is a particularly useful in solubilizing vinyl based resins. Resins based on vinyl produce jet inks with strong affinity to polyvinyl chloride wire jacketing materials. The combination of resin and solvent can be associated with a soft pigment providing

[1] Sweet-Cumming patent, No. 3,373,437 issued March 12, 1968

a jet ink that does not require agitation in the ink jet printer to keep the composition consistent. The system bonds to the surface of the wire jacket, resisting transfer when wire is rolled directly after the printing process. The speed of evaporation for MEK makes it ideal for creating resilient inks with rapid drying characteristics. The draw back to MEK use has been its regulatory status as hazardous air pollutant (HAP) and a volatile organic compound (VOC).

On December 19, 2005, the U. S. Environmental Protection Agency removed butanone from the list of hazardous air pollutants (HAPs). After technical review and consideration of public comments, EPA concluded that potential exposures to butanone emitted from industrial processes may not reasonably be anticipated to cause human health or environmental problems. Emissions of butanone will continue to be regulated as a volatile organic compound because of its contribution to the formation of tropospheric (ground-level) ozone.[2] Despite this change in status, MEK remains a volatile organic compound (VOC) subject to regulation.

Volatile organic compounds (VOCs):

Organic chemicals all contain the element carbon (C); organic chemicals are the basic chemicals found in living things and in products derived from living things, such as coal, petroleum and refined petroleum products. Many of the organic chemicals we use do not occur in Nature, but were synthesized by chemists in laboratories. *Volatile* chemicals produce *vapors* readily; at room temperature and normal atmospheric pressure, vapors escape easily from volatile liquid chemicals. Volatile organic chemicals include gasoline, industrial chemicals such as benzene, solvents such as toluene and xylene, and tetrachloroethylene (perchloroethylene), the principal dry cleaning solvent. These materials are linked to the formation of smog. In addition, some VOC's such as formaldehyde and ethylene may harm plants.

Companies emitting large volumes of VOC's are required to obtain permits. The permitting process can be time consuming and expensive. Many manufacturing facilities will have several sources of VOC's in their normal production environment. For example: Bakeries emit large volumes of ethanol as a by-product of bread production. Wire & cable production facilities emit VOC's from the wire extrusion process. In this situation, removing/reducing VOC's from ink jet fluids may allow the production plant to reduce the level of permitting required. When ink jet fluids are the only source of VOC's, elimination/reduction of reportable VOC's is highly desirable.

South Coast Air Quality Management District (SCAQMD) in California is further restricting the use of VOC's with by implementing Rule 1171 which impacts the cleaning of ink jet printers in their jurisdiction.

Rule 1171:

This rule was designed by the SCAQMD to reduce VOC emissions by 7.5 tons/day, when fully implemented. The efforts started in 1991 and are aimed at ozone reduction in southern California. Rule 1171 has been expanded via amendments to cover all solvent cleaning activities in all facilities. Some applications are still exempt in 2005, but they do NOT include ink jet printers. The rule affects cleaning of electrical apparatus/electronic components, coating/adhesive application and cleaning certain ink application equipment.

"The cleaning of inkjet printers falls under Rule 1171(c)(l)(D)(i), "General Cleaning of Ink Application Equipment". In fact, section (h)(7) clearly specifies the applicability of section (c)(l)(D)(i) to the cleaning of ink application equipment used in inkjet printing. The VOC limit for solvents used in this cleaning application is 25 g/l beginning July 1, 2005."

"For inkjet printing, the cleaning process typically involves the removal of uncured ink from the inkjet print heads using solvents. Removal of cured ink is currently exempt from the requirements of Rule 1171. Uncured inks are removed from the print heads by wipe cleaning with solvent, performing "ink purging" where solvent is fed into the print heads, or by rinsing the print heads with solvent (in squirt bottles) and some brushing to aid in the cleaning process. Recycling of solvent through the machine to maintain ink viscosity is not considered part of the cleaning process."

"Staff is aware of facilities that currently comply with the requirements of Rule 1171 for cleaning ink jet printing equipment. Acetone, a VOC-exempt compound, has successfully replaced the VOC solvents previously used to remove uncured ink from print heads. One facility has also implemented changes to its cleaning procedure for long-term equipment shutdown. Additionally, Rule 1171 allows the option of using an emission control device for facilities to use VOC solvents for cleaning."[3]

Based on this information, the automatic cleaning cycle used in ink jet printing equipment falls under the regulation. The cleaning cycle uses make up through the printhead. Using a make up that fulfills the regulation would contaminate inks based on Methyl Ethyl Ketone.

Conclusion:

To retain the desirable characteristics of MEK based ink jet fluids without the impact of VOC emissions regulations, a replacement, non-regulated group of solvents needs to be indentified and used. Any characteristics of the printer which also reduces the evaporation of volatile solvents into the air will also reduce the impact of solvent emissions.

Acetone ((CH3)2CO) provides an alternative to without the same regulatory impact. It can be used an alternative to create a stable quick drying ink jet fluid capable of printing a variety of jacketing materials.

Acetone is listed as an organic compound exempt from VOC regulation by the EPA. 4 Solvents are designated as exempt based on negligible photo chemical reactivity. The evaporation rate of acetone makes it a suitable alternative for high speed production environments. Inclusion of this solvent in ink jet formulas allows the corresponding make up/solvent to be exempt as well. Make up/solvents with less than 1% VOC fulfill the requirements of SCAQMD for cleaning ink jet printers in California (Rule 1171). Make up/solvent used with ink jet printers can be eliminated from the plants emissions reporting.

Printing equipment which reduces to release of solvent fumes into the environment further reduces the impact of VOC's. The current Metronic printer contains a system for re-condensing solvent fumes produced during the ink jet process and reusing them in the system. As stated earlier, two types of fluids are used in the operation of an ink jet printer: ink and make up/solvent. The printer draws ink from the supply container into a mix tank to replace ink drops sent to the surface during printing. The printer draws make up/solvent from the supply container and adds it to the mix tank to replace solvent lost to evaporation during the printing process. The mixing tank feeds fluid to the printhead. This fluid is moved via a gear pump, under pressure, to the printhead. Air space between the top of the fluid and the top of the mix tank contains solvent fumes. This area is exhausted though a solvent recovery system containing a heat sink and fan. Solvent fumes are condensed into liquid form and added to the supply bottle of make up/additive contained in the printer. In this manner, solvent loss to the atmosphere is reduced. ■

[2] Modifications To The 112(b)1 Hazardous Air Pollutants, Environmental Protection Agency, 70 FR 75047

[3] From Staff Report for Proposed Amended Rule 1171-Solvent Cleaning Operations, South Coast Air Quality Management District, April 19, 2005

[4] 40 CFR51.100(s), revised as of 7/1/2003