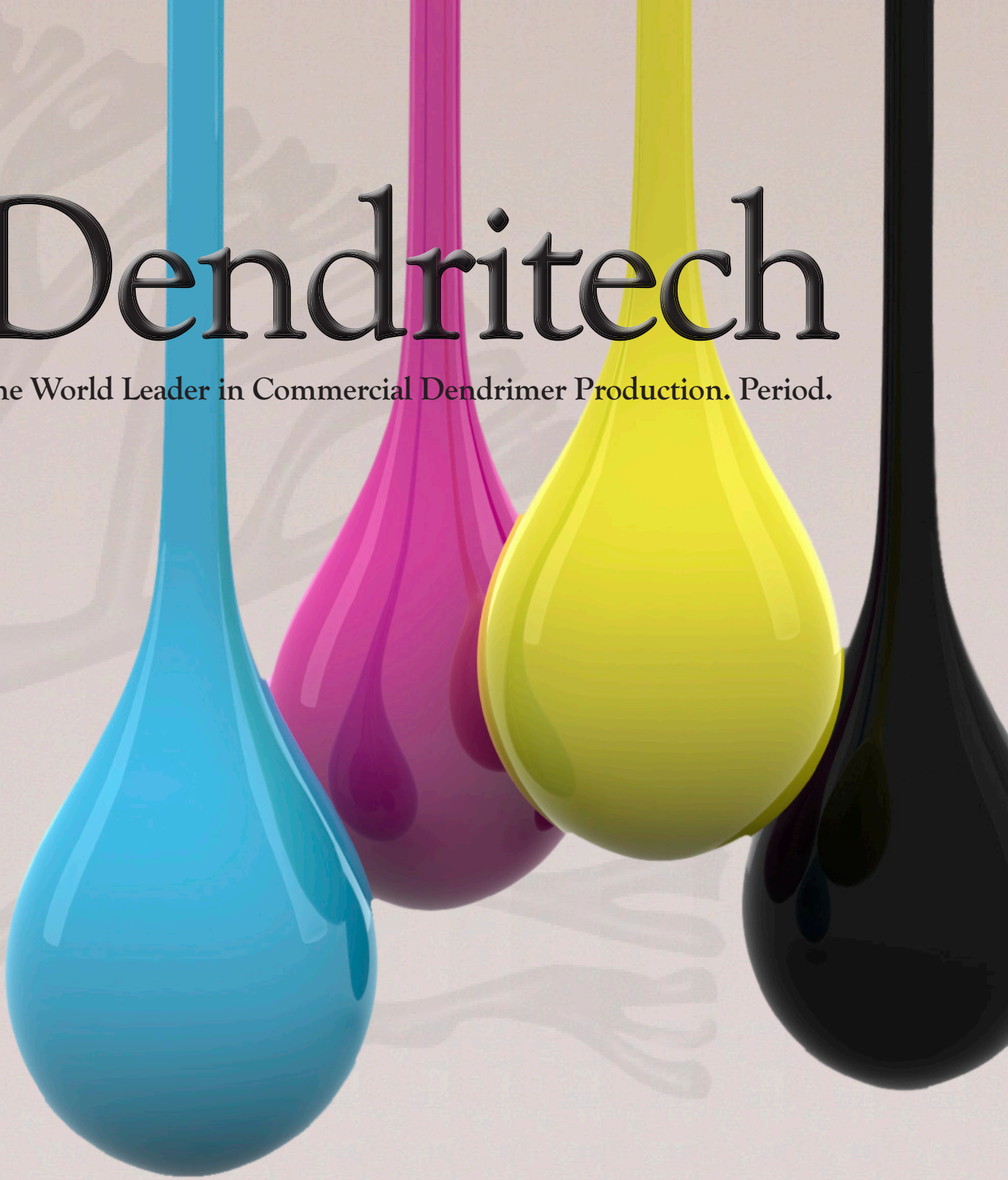
Dendritech

The World Leader in Commercial Dendrimer Production. Period.



PAMAM Dendrimers in Inkjet Printing

Polyamidoamine (PAMAM) Dendrimers in Inkjet Inks

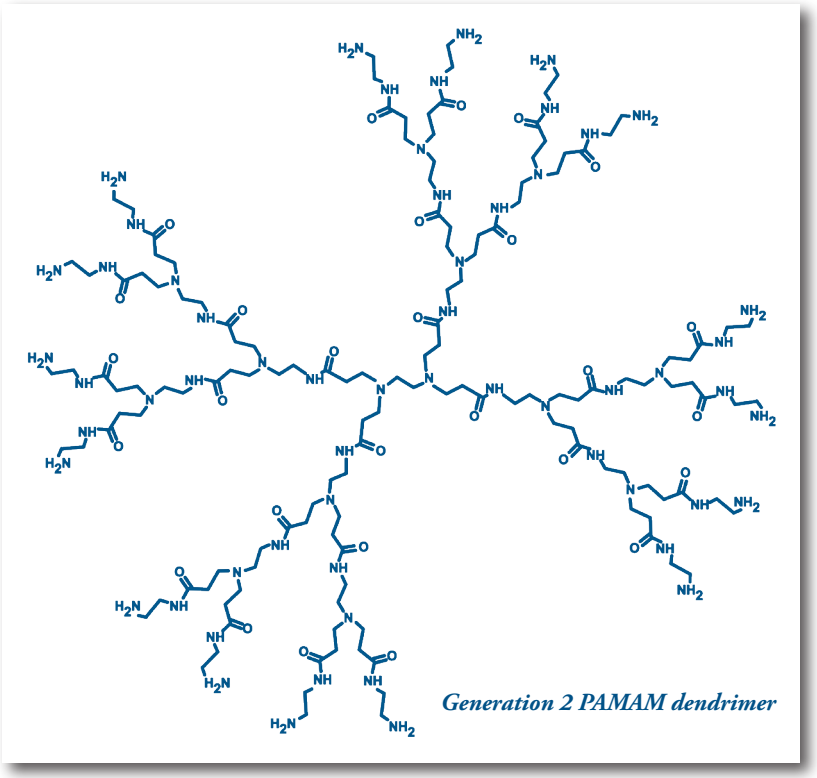
In both industrial coding and marking and desktop inkjet printing, PAMAM dendrimers are a versatile performance additive that can improve ink adhesion, waterfastness, rub-off resistance, color characteristics and print quality on porous and nonporous substrates with reliable, consistent performance.

Background

Dendrimers represent a class of polymer architecture known for their nanoscopic size, molecular uniformity, "compact" globular shape and high chemical functionality (both exterior and interior).[1]

The PAMAM (polyamidoamine) dendrimers are the most widely studied type and have been commercially supplied by Dendritech, Inc. since 1994 into both industrial and biomedical applications. Compared to other dendrimers or hyperbranched polymers, the PAMAM dendrimers have the longest term of successful commercial applications. These highly ordered, branched polymers are used as additives in ink formulations (0.5-2% level) to enhance adhesion to a variety of substrates, improve waterfastness, and provide excellent film color characteristics while maintaining ink formulation stability and reliable printer operation.

Lower "generation" (molecular weight) PAMAM dendrimers are particularly effective and their Newtonian viscosity characteristics in solution, solubility in polar solvents (tailorable) and their amorphous, noncrystallizing nature provide for formulation flexibility and reproducible ink application characteristics. In fact, their highly functional "molecular Velcro" surface and molecular uniformity facilitate their use even in micro- and nano-lithography applications.



Generation 2 PAMAM dendrimer

PAMAM (Polyamidoamine) Dendrimers

Dendrimers consist of a core, branching units, and terminal surface groups. These three structural components can be tailored to provide a scaffold that can be tailored for specific applications.

PAMAM dendrimers are manufactured from common industrial raw materials by an iterative, divergent growth process where each successive "generation" of polymers provides an approximate doubling of molecular weight and terminal surface functionality.

The PAMAM dendrimers are the most well-known family of dendritic polymers and are commercially based on an ethylenediamine core, an amidoamine repetitive branching structure and a terminal primary amine surface.

Selected properties of Dendritech's PAMAM Dendrimers Ethylenediamine Core Primary Amine Surface*

Generation Number	Molecular Weight	Measured Diameter (nm)	Surface Groups
0	517	1.5	4
1	1,430	2.2	8
2	3,256	2.9	16

- ***Ideal structure; not to be used as specifications**
- **Note: Higher generations are available; contact Dendritech**
- **Technical grade dendrimers are supplied for optimum cost/performance in ink formulations**

The high density of functional exterior groups is particularly important as this polyvalency provides multiple interactions with many surfaces and can strongly link ink colorants (both dye and pigment-based) to them. An idealized chemical structure of a Generation 2 PAMAM dendrimer is shown here, illustrating the internal amidoamine branching units and the sixteen primary amine terminal groups.

Features and Benefits in Inkjet Inks

PAMAM dendrimers have a number of attractive, commercially demonstrated properties useful in ink formulations. They have broad applicability in both continuous and drop-on-demand printers and can improve coating robustness and film characteristics on many substrates including plain/coated papers, glass, metals and plastics. In most cases, simple mixing of the dendrimer into the ink formulation is sufficient. **Low use levels of 0.5-2.0% by weight are effective with both dye and pigment colorants.** Specific features and benefits include:

FEATURE	BENEFIT
High number of terminal functional groups (primary amines) on a compact molecular structure, which can be modified to provide a variety of surface functionalities. Cationic (e.g. primary amine), anionic (e.g. carboxylate), neutral (e.g. hydroxy) or hydrophobic (hydrocarbon) exterior groups are examples, as are "mixed" surfaces to provide customized characteristics.	Strong, polyvalent adhesion to a variety of porous and nonporous substrates to provide robust, water-resistant films with excellent opacity, color and print characteristics. Tailorable properties for optimum solubility, humectantcy, latency, and coating characteristics.
Highly organized polymer with defined shape, size, polydispersity and interstitial volume	Reliable and consistent performance in ink formulations – every time
Newtonian viscosity/shear rate insensitive in solution due to nanoscopic size and globular shape. Solution viscosity is lower than linear polymers of similar molecular weight but "dry" polymer has high viscosity/adherence	Formulation flexibility, consistent viscosity and reliable jetting characteristics even in high-speed printers.
Noncrystalline, amorphous polymer characteristics	No plugging from polymer solids and "dry" polymer remains as a highly viscous but soluble humectant liquid amenable to cleanout
Highly hydrophilic and very soluble in water, alcohols and glycols, but solvent solubility characteristics readily altered by modification of exterior functional groups	PAMAM dendrimers can be tailored to required performance specifications
Designed, precision scaffold to attach dye moieties or modify pigment dispersion characteristics.	Improved ink formulation stability and ink coating characteristics
Ability to form ionic, metal or semiconductor nanocomposites and pattern defined features on a variety of surfaces	Internal "container" properties of the PAMAM structure can be utilized for precise placement of nanoparticles (including nanolithography)
Low acute toxicity, irritation and sensitivity potential; high "biofriendliness"	PAMAM dendrimer mildness is well known in biomedical applications and is unique for a primary amine polymer

Selected PAMAM Dendrimer References

The following summary of PAMAM dendrimer utility in inkjet inks is not meant to be comprehensive, but illustrative references of the benefits cited above for both desktop and continuous inkjet printing, on porous and nonporous substrates:

• Low-generation PAMAM dendrimers can be added to dye-based aqueous inkjet inks to improve coating characteristics on plain paper, coated paper and transparency film. Printed images resist feathering and bleeding and waterfastness is improved.[2] Similar results can be seen with fluorescent ink formulations for security marking where waterfastness of porphyrin dyes was improved.[3] and in mixtures with other amines.[4]

In all of these examples, typical levels of 0.5-2.0% dendrimer by weight in the formulations were effective.

• The PAMAM amine surface groups could also be modified with polyethyleneoxy-side chains to improve the ink latency.[5] Additionally, use of these dendrimers was taught for radiation-curable ink formulations to provide adhesion, water resistance and cold and hot humidity resistance.[6,7]

• PAMAM dendrimers were also effective adhesion promoters in continuous inkjet ink formulations in high-speed printing and marking. Mixing in the dendrimer improved adhesion and gave water-resistant ink coatings with excellent ruboff resistance and visual intensity. A variety of dyes and pigments could be used, and the markings were durable on a broad range of substrates including glass, metal, plastic and rubber surfaces.[8]

• A hydrophobic "mixed surface" PAMAM dendrimer was illustrated for high-speed marking of wet glass surfaces and provided excellent ruboff and water resistance.[9] Similarly, dendrimer-containing ink formulations with or without silanes were used to effectively adhere to a wide variety of nonporous glass, metal and plastic surfaces.[10]

• PAMAM dendrimers are also effective carriers of other materials via their high number of readily-modified surface groups[11]. More specifically, reactive dyes can be covalently linked to low-generation PAMAM dendrimers and formulated into inkjet inks.[12] As inkjet technology becomes ever more refined, it is expanding into nontraditional applications such as printing of circuitry with conductive or semiconductive inks.

Finally, micro- and nano-lithography applications by stamping or "dip pen" techniques are also being widely investigated. The unparalled uniformity, nanomolecular size, and "container" properties of PAMAM dendrimers suggest their use in these areas, including the ability to precisely deposit metallic nanoparticles on surfaces in a highly organized fashion.

Product Characteristics

Physically, PAMAM dendrimers are somewhat viscous liquids when supplied in solution (methanol is the "default" solvent; contact Dendritech for other solvent options), but when "dry" they are extremely viscous, amorphous syrups depending on degree of solvation.

Unmodified, primary amine-surface PAMAM dendrimers are hygroscopic, hydrophilic, and are miscible in water, lower alcohols and glycols. They can be hydrophobically modified to achieve solubility in less polar solvents (e.g. ketones; glycol ethers) and even hydrocarbon solvents if desired. PAMAM dendrimers have a high concentration of primary amines on the surface and tertiary amines and amide groups in the interior branching units. The pKa of the primary amines is around 9.5, while that of the less basic tertiary amines is 5.5.

Selected References

1. US Patent 4,507,466 (Tomalia, et.al.); *Dense Star Polymers Having Cores, Core Branches, Terminal Groups*; The Dow Chemical Company (3/26/85)
2. US Patent 5,120,361 (Winnik, et.al); *Ink Compositions*; Xerox Corporation (6/9/92)
3. US Patent 5,256,193 (Winnik, et.al.); *Porphyrin Chromophore and Dendrimer Ink Composition*; Xerox Corporation (10/26/93)
4. US Patent 5,254,159 (Gundlach, et.al); *Ink Compositions*; Xerox Corporation (10/19/1993)
5. US Patent 5,266,106 (Winnek, et.al.): *Ink Compositions with Dendrimer Grafts*; Xerox Corporation (11/30/93)
6. US Patent 6,300,388 B1 (Verdonck; Vanmaele); *Ink Compositions for Ink Jet Printing*; Agfa-Gevaert (10/9/2001)
7. US Patent 6,310,115 (Vanmaele; Verdonck); *Ink Compositions for Ink Jet Printing*; Agfa-Gevaert (10/30/2001)
8. US Patent 5,596,027 (Mead et.al.); *Condensation and Water Resistant Jet Ink*; Videojet Systems International, Inc. (1/21/97)
9. US 6,221,933 B1 (Zhu et.al.); *Fast Drying Jet Ink Composition*; Marconi Data Systems Inc.; (4/24/01)
10. US 6,251,175 B1 (Zhu; Siddiqui); *Jet Ink Composition*; Marconi Data Systems Inc. (6/26/01)
11. US 5,338,532 (Tomalia et.al.); *Starburst Conjugates*; The Dow Chemical Company (8/16/94)
12. US Patent 5,098,475 (Winnik, et.al.); *Inks with Dendrimer Colorants*; Xerox Corporation (3/24/92)

Dendritech was the first company to commercially supply dendrimers and has a dedicated production facility specifically designed to manufacture PAMAM dendrimers. Located in Midland, Michigan, we have been supplying dendrimers to a variety of leading industrial and biomedical customers since 1994.

Dendritech is committed to reliable supply of PAMAM dendrimers (it's what we do, every day) and closely works with customers to optimize dendrimers for their specific needs. Whether grams or kilograms, contact Dendritech and tell us what you need. We'll listen.

More details can be found on the Dendritech website at *www.dendritech.com*.

Dendritech, Inc.
3110 Schuette Drive
Midland, MI 48642
PH: 989.496.1152
FAX: 989.496.2051
EMAIL: scheibert@dendritech.com
WEB: www.dendritech.com