Examination of Gel Pen Inks Using Physical and Thin Layer Chromatographic Examination

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The use of thin layer chromatography (TLC) in the examination of writing materials is well documented and a proven technique. As technology continues to develop new and better methods of manufacture, those methods will permeate society and give rise to different products. This has occurred within the field of writing materials, as both instruments and inks have changed over time from nib pens to ball pens and from natural inks of iron to inks of pigment suspensions in water-based polymer gels. This most recent development, gel pens, combines ball pens with pigmented polymer gel ink. The gel pen presents a challenge to the forensic examiner, which is addressed initially with this study, including both traditional physical examinations, chemical spot tests, and TLC. A total of 98 different samples of gel pens were examined and yielded examination results that provided for discrete discrimination of over 35% of the gel pens.

Introduction

The use of thin layer chromatography (TLC) in the examination of writing materials is well documented and a proven technique (Brunelle and Pro, 1972; Clement and Ceccaldi, 1981; Jasuja and Singla, 1990 and 1995; Lewis, 1996.) As technology continues to develop new and better methods of manufacture, those methods will permeate society and give rise to different products. This has occurred within the field of writing materials, as both instruments and inks have changed over time from nib pens to ball pens and from natural inks of iron to inks of pigment suspensions in water-based polymer gels. This most recent development, gel pens, combines ball pens with pigmented polymer gel ink (Gernandt and Urlaub, 1996). The gel pen presents a challenge to the forensic examiner, which is addressed initially with this study, including both traditional physical examinations (Dick, 1970; Chowdry, Gupta, and Bami, 1973; Day, 1985; Sensi and Cantu, 1982), chemical spot tests, and TLC.

Materials and Methods

Ninety-eight different gel pens were collected from sources in India, Europe, and the United States. Writings on plain white bond paper were prepared with each pen, and a series of physical examinations were conducted, followed by TLC. Visual examination required magnification of 10X, and ultraviolet (UV) examination required both long- and short-wavelength lamps (254 nm and 365 nm). Review of the writings was also performed with a video-based infrared reflectance and luminescence employing a Wratten 87 filter and Schott BG-18 excitation filter. Solubility testing was conducted with a range of reagent-grade solvents (distilled water, methanol, acetone, chloroform, and pyridine). Precoated silica gel plates from Merck (Darmstadt, Germany) were used for the TLC. Reagent-grade solvents were used for TLC solvent systems: butanol, acetone, ethyl acetate, methanol, acetic acid, ethanol, pyridine, ethyl methyl ketone, and chloroform.

Ink Manufacturer	Colors of Ink
Wright-A-One	Red
Montex	Blue, Green, Red, Black
Add Gel	Black, Blue
Pentel	Red, Blue, Black, Pink, Purple
Hero	Blue
Reynolds	Blue
Cell Pointec	Golden, Blue
Schefields	Blue, Silver
Rotomac	Blue
Linc Hi School	Blue
Stic Geltra	Blue
Uniball	Black, Silver (Orange, Blue, Green, Violet)
Zebra	Blue, Multicolored, Copper, Silver, Black, Golden, Blue-green, Pink, Purple, Green
Bic	Pink, Silver, Green, Golden, Blue
Sakura	Blue, Purple, Red, Black, Dark Green, Metallic (Purple, Red, Black, Green, Pink, Brown, Light Blue, Dark Blue, Light Green)
Papermate	Black, Blue, Red, Purple, Pink, Green, Orange
Pilot	Green, Blue, Black, Red
Mon Ami	Red
Rose Art	Metallic (Gold, Green, Orange, Blue, Pink, Purple)
Sanford	Black, Blue, Red

Table 1. Manufacturers and colors of ink tested. Note that some manufacturers had multiple samples of the same color.

Results and Discussion

The 98 gel pen samples were produced by 20 different manufacturers and represented 13 different colors (Table 1). Metallic colors were also present from most of the manufacturers.

Examination with both short- and long-wave UV resulted in very little response. Samples manufactured by Uniball, Signo, and Zebra (except black) gave off a copper color upon exposure to short UV. Pink samples from Zebra, Pentel, and Papermate fluoresced pink in both long- and short-wave UV. Orange samples from Pentel and Papermate fluoresced pink in short-wave UV and orange in long-wave UV. Papermate green gel ink fluoresced light green in both long- and short-wave UV (Table 2).

Results of solubility testing (Table 3) of the gel inks in distilled water, acetone, methanol, chloroform, and pyridine were documented by indicating the manufacturers whose inks were soluble in each of the tested solvents. Of the inks tested, 58 were found to be soluble in at least 1 of the solvents and many in multiple solvents. Methanol and acetone were the best solvents for 27 and 25 inks respectively.

A total of 13 different TLC solvent systems were investigated, and 2 TLC solvent systems were found to be useful in differentiating the soluble gel inks. These were System I: butanol:ethanol:water:acetic acid (60:20:20:0.5) and System II: butanol:ethanol:water (50:25:25). The results of the TLC examinations (Table 4) were documented by indicating the ink examined and the number and color of spots visible under both white and UV light (both 254 nm and 356 nm).

Conclusions

The use of classical physical nondestructive analysis techniques in conjunction with TLC has

Manufacturer	Color	Infrared Reflectance	Infrared Luminescence
Wright-A-One	Blue	Transparent	None
Montex	Blue, Black, Red	Transparent	None
Montex	Blue, Green	Transparent	Positive
Add Gel	Black	Transparent	None
Add Gel	Blue	Transparent	Positive
Pentel	Blue, Red	Transparent	None
Pentel	Black	Opaque	None
Pentel	Pink, Purple	Luminescent	Positive (++)
Hero	Blue	Opaque	None
Reynolds	Blue	Opaque	None
Cell Pointec	Golden, Blue	Opaque	None
Schefields	Blue, Silver	Opaque	None
Rotomac	Blue	Transparent	Positive
Rotomac	Blue	Opaque	None
Linc Hi School	Blue	Opaque	None
Uniball	Black, Silver Orange, Silver Blue	Opaque	None
Uniball	Silver Violet	Opaque	Positive
Uniball	Silver Green	Opaque	Positive Halo
Zebra	Copper, Silver, Black, Golden, Blue, Green	Opaque	None
Zebra	Multicolored, Blue-green, Pink, Purple	Luminescent	Positive (++)
Bic	Pink, Silver, Green, Golden, Blue	Opaque	None
Sakura	Blue, Black, Dark Green, Metallic (Black, Red, Purple, Green, Gold, Pink, Brown, Light Blue)	Opaque	None
Sakura	Purple, Red	Transparent	Positive
Sakura	Blue	Almost Transparent	None
Papermate	Black, Blue	Opaque	None
Papermate	Green	Transparent	None
Papermate	Purple, Pink, Orange	Transparent	Positive
Pilot	Black, Blue	Almost Transparent	None
Pilot	Green, Red	Transparent	None
Mon Ami	Red	Transparent	None
Sanford	Black, Blue	Opaque	None
Sanford	Red	Transparent	None
Rose Art	Metallic (Blue, Green)	Opaque	None
Rose Art	Metallic (Orange, Gold, Purple)	Transparent	None
Rose Art	Pink Metallic	Transparent	Positive

Table 2. Illustrates the results of the infrared reflectance and luminescence examinations. Note that several companies make formulations of the same color with different characteristics. Also note that most black inks were indistinguishable with this test.

Water	Acetone	Chloroform	Pyridine	Methanol
Montex, Add Gel, Rotomac, Uniball, Pilot	Wright-A-One, Montex, Add Gel, Bic, Cell Pointec, Zebra, Pentel, Pilot, Papermate, Sanford	Montex, Pentel, Add Gel, Cell Pointec, Zebra, Bic, Mon Ami, Pentel, Rose Art, Papermate, Sanford, Sakura	Montex, Add Gel, Cell Pointec, Zebra, Mon Ami, Pentel, Sanford, Sakura	Wright-A-One, Montex, Add Gel, Rotomac, Uniball, Zebra, Pilot, Pentel, Papermate

Table 3. Solubility of ink by manufacturer and solvent.

resulted in a preliminary examination scheme of value in the differentiation of gel pen inks. It is clear, due to the nature of gel pen inks, that this scheme will not differentiate all inks and thus is not adequate to use in association with a standard reference library of such inks. It is proposed that an additional examination methodology be investigated to include instrumental examination by SEM/EDAX, FTIR, and Raman spectroscopy. This investigation is under way and should be reported in the near future.

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Ink	White Light	254nm	356nm	Rf Value
Wright-A-One, Red	Orange	Bright Yellow	Bright Yellow	0.98 (0.82)
Montex Hycute, Blue	Purple Blue			0.57 (0.61) 0.34 (0.29)
Montex Hyspeed, Blue	Purple Blue			0.55 (0.61) 0.32 (0.44)
Montex, Green	Blue			0.22 (0.36)
Montex, Blue	Blue Green Blue			0.79 0.70
Add Gel, Black	Blue (Grey) (Dark Grey)			0.75 (0.87) (0.84) (0.64)
Add Gel, Blue	Pink Blue	Pink	Pink	0.65 (0.41) 0.31 (0.32)
Add Gel, Blue	Pink Blue	Pink	Pink	0.42 (0.39) 0.27 (0.33)
Add Gel, Blue	Blue	Pink	Pink	0.44 (0.34) 0.54 (0.43)
Add Gel, Blue	Blue	Pink	Pink	0.35 0.50
Add Gel, Blue	Blue (Purple)	(Pink)		0.74(0.29) (0.39) (0.82)
Add Gel, Blue	Blue			0.79 (0.84)
Add Gel, Blue	Blue Purple			0.35 (0.38) 0.56 (0.85)
Rotomac, Blue	Purple Blue (Blue)			0.53 0.34 (0.39)
Uniball, Silver-Violet	Pink Pink Blue	Pink Pink	Pink Pink	0.73 0.59 0.46
Uniball, Silver-Orange	Orange			0.80
Uniball, Silver-Green	Blue			0.34
Uniball, Silver-Blue	Blue			0.32
Zebra, Blue	Blue			0.30
Zebra, Copper	Pink			0.86
Zebra, Blue-Green	Green			0.31
Bic, Metallic Pink	Pink			0.73
Pilot, Green	Blue			0.30
Pilot, Blue	Blue			0.79
Zebra, Pink	Pink			0.64
Zebra, Purple	Purple			0.50
Pentel, Red	Pink	Orange	Orange	0.51
Papermate, Red	Pink			0.68
Pentel, Purple	Purple			0.62
Sanford, Red	Pink			0.70
Pilot, Red	Pink Pink	Orange Yellow	Orange Yellow	0.84 0.72
Papermate, Purple	Purple			0.58

Table 4. TLC results using solvent System I and solvent System II. The results of System II that differed from System I are shown in parenthesis.