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# DIFFERENTIATION OF BLUE BALLPOINT PEN INKS*

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In the United States, at least four out of five persons use a ballpoint pen for routine writing, rather than a fluid ink pen. This tremendous change in writing instrument preference has occurred in the past fifteen years, and there is no indication of a reversal of the trend. Accordingly, problems of differentiating ballpen ink, especially blue ballpen ink, are being met increasingly in the laboratory.

A review of the literature indicates that none of the known methods of differentiating ballpen inks is based on specific constituents. All of the non-optical methods involve either the removal of ink from the document, followed by chromatography, or spotting the ink line with various reagents for empirical differentiation (1–7).

While some reagents will differentiate many different classes of ballpoint pen inks, empirical spot testing is inconclusive if a reagent fails to affect the inks, or if it gives similar reactions with all or several classes of inks. Spot testing, to be productive, should be based upon known reactions with specific constituents, where their presence or absence will have definite class significance.

The present chromatographic methods are limited by the amount of dyestuff that reasonably can be removed. Furthermore, pigments present in the ballpen inks are frequently insoluble in solvents that remove dyes. Although a more representative sample of all dyestuffs in an ink formulation may be scraped from a document, the pigments in the ink are subject to the same problem of insolubility in the solvent or solvents for chromatography. Martin's use of acetone (7) is a case in point. An ink formulation containing phthalocyanine blue, methyl violet, and Victoria blue would produce a chromatogram indicating only methyl violet and Victoria blue, because of the minimal effects of acetone on a pigment such as phthalocyanine blue. In addition, not all dyestuffs are separated by any one solvent or solvent system, and the presence of several dyes might be overlooked if these dyes do not separate with a certain solvent or combination of solvents.

The two broad groups of substances involved in ballpen inks are the vehicle and the dyestuffs. Tests based upon the presence or absence of various types or varieties of these constituents would allow ballpen ink differentiation to be more definitive and less empirical.

The experimental data below, upon which a scheme for the presumptive identification of blue ballpen ink dyestuffs and ink formulations is based, has been used successfully in over fifty cases in the past year by the San Francisco Identification Laboratory of the U. S. Postal Inspection Service.

## EXPERIMENTAL DATA

A total of 210 pens and/or refills were used in this study. These include pens available in the San Francisco area during the years 1957 through 1959 and additional pens obtained from a cross-section of ballpoint pen suppliers and users, domestic and foreign, by the San Francisco Labora-

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TABLE 1

COLOR DISTRIBUTION—CHROMATOGRAPHIC

| Number of Pens | Pigment (Insoluble) | Dye (Soluble) | Dye (Soluble) |
|---|---|---|---|
| 32 | — | blue | purple |
| 2 | — | blue | — |
| 1 | — | blue | dark purple |
| 1 | blue | purple | — |
| 22 | green-blue | purple | — |
| 8 | green-blue | blue | — |
| 3 | green-blue | red (fluorescent) | — |
| 2 | green-blue | blue | red (fluorescent) |
| 21 | green-blue | purple | blue |
| 21 | green-blue | blue | red (fluorescent) |
| 4 | green-blue | blue | blue |

tory of the U. S. Postal Inspection Service. While the sample used is small in view of the millions of ballpoint pens in use today, it is believed to be representative. It is known that ballpoint pen manufacturers may not produce their own cartridges and that one ink formulation may be encountered under numerous brand names.

Horizontal chromatography was utilized to separate the dyestuff constituents of the test pens. Ink lines were drawn on strips of Whatman No. 1 paper and chromatographed with various solvents including ethyl alcohol (absolute), lacquer thinner, and ethyl alcohol (10:1), nitroethane, and a mixture of nitroethane with ethyl alcohol and lacquer thinner. It was found that no one solvent or combination of solvents separated all the dyestuffs in the inks. Table 1 shows the distribution of color bands obtained from the first 117 pens tests in 1957–1959.

A study of the literature indicated various dyestuff possibilities for each of the above listed pigment and dyestuff color groups (2, 8–12):

a. Green-blue pigment—phthalocyanines
b. Blue pigment—iron blues, ultramarine blues
c. Blue dyes—Victoria blues, alkali blues, soluble phthalocyanines
d. Red dyes with bright pink fluorescence—rhodamine B, eosins
e. Violet and purple dyes—methyl violets, crystal violet, indulines

These dyestuff names should not be considered as representing specific chemical compounds with formulas, such as is the case with most other organic and inorganic substances. Aspirin will always be acetylsalicylic acid; however, the term phthalocyanine blue includes various individual compounds. Dyestuffs can be grouped into types, varieties, or groups, according to dyeing properties and/or chemical properties. Not all dyestuffs giving similar reactions will have the identical chemical formula because of differences in substituent groups and/or manufacturing methods, yet the group as a whole will have certain properties and characteristics which will set it apart from other dyestuff groups or classes.

The following listed reactions serve to differentiate the above mentioned classes of dyestuffs (13–15):

a. *Phthalocyanines*—yield a bright green color with hydrochloric and sulfuric acid, and ignition of the dyestuff gives a green flame indicating copper.

b. *Iron blues*—give a positive iron test with hydrochloric acid and potassium thiocyanate.

c. *Ultramarines*—acids release hydrogen sulfide which is detectable with lead acetate paper.

d. *Alkali blues*—not affected by hydrochloric acid, but give a reddish brown color with sodium hydroxide.

e. *Victoria blues*—give brownish reactions with both acids and bases.

f. *Rhodamine B*—unaffected by sodium hydroxide, decolorized to a faint orange yellow with hydrochloric acid, bright pink fluorescence.

g. *Eosins*—give an orange coloration with sodium hydroxide and decolorize to a faint yellow with hydrochloric acid.

h. *Methyl violets* (and crystal violet)—yellowish brown reactions with hydrochloric acid, restored to purple by addition at a base.

i. *Indulines*—not decolorized by either bases or acids.

Tests with 41 different varieties of the above listed types of dyestuffs confirmed these reactions.

The various dyestuff bands obtained by the chromatography of the fluid inks were tested, using the listed test methods. *In all cases, typical reactions of the dyestuff class were observed. The reactions are considered to provide presumptive rather than absolute identification.* Table 2 sets forth the presumptive constituents of the first 117 pens tested.

It is noted that the principal constituents, phthalocyanines, methyl violet, alkali blue, Victoria blue, and rhodamine B are all relatively cheap, commonly available, dyestuffs.

TABLE 2

PRESUMPTIVE DYESTUFF CONSTITUENTS

| Number of Pens | Presumptive Constituents |
|---|---|
| 32 | Victoria blue and methyl violet |
| 2 | Victoria blue |
| 1 | Victoria blue and indulin |
| 1 | Iron blue and methyl violet |
| 22 | Phthalocyanine blue and methyl violet |
| 8 | Phthalocyanine blue and alkali blue |
| 3 | Phthalocyanine blue and rhodamine B |
| 2 | Phthalocyanine blue, soluble phthalocyanine blue and rhodamine B |
| 21 | Phthalocyanine blue, methyl violet and Victoria blue |
| 21 | Phthalocyanine, Victoria blue, and rhodamine B |
| 4 | Phthalocyanine blue, Victoria blue and alkali blue |

Table 3, an additional 93 pens collected in 1960 by the Postal Inspection Service, reveals the number of pens with the indicated presumptive dyestuff constituents.

The predominance of the methyl violet—Victoria blue formulation among the 1960 group of pens appears rather significant. The combinations (a) phthalocyanine blue, methyl violet, and alkali blue; (b) phthalocyanine blue, methyl violet, and rhodamine B; (c) phthalocyanine, alkali blue, and rhodamine B; (d) phthalocyanine blue and Victoria blue; (e) alkali blue and rhodamine B; (f) alkali blue and methyl violet; (g) Victoria blue and rhodamine B; were not observed in any of the 210 test pens. It is expected that for tinctorial and/or manufacturing reasons these dyestuff combinations are not in normal use.

Because of the problems inherent in chromatography, attention was given to spot testing directly on the ink line. Since the presumptive dyestuff constituents of the test pens had already been established, comparisons could be made between the spot test results and the known constituents. It was established that when a small drop of concentrated hydrochloric acid was spotted on an ink line with a micropipette, a greenish or olive coloration of the ink line itself resulted if any phthalocyanine blue dyestuff was present. Non-phthalocyanine inks never gave this effect. In some cases, dyes "bled" into the hydrochloric acid drop, i.e., the dyestuff dissolved in the hydrochloric acid.

TABLE 3

PRESUMPTIVE DYESTUFF CONSTITUENTS

| Number of Pens | Presumptive Constituents |
|---|---|
| 3 | Victoria blue |
| 49 | Victoria blue and methyl violet |
| 2 | Phthalocyanine blue and rhodamine B |
| 10 | Phthalocyanine blue, Victoria blue and rhodamine B |
| 7 | Phthalocyanine blue and alkali blue |
| 13 | Phthalocyanine blue and methyl violet |
| 9 | Phthalocyanine blue, methyl violet and Victoria blue |

Experiments with non-phthalocyanine blue inks revealed that when a strip of filter paper was placed on the HCl spot and rubbed slightly to absorb all the hydrochloric acid, the absorbed liquid, neutralized with a saturated solution of sodium bicarbonate, allowed the reconstituted colors to be observed. Inks containing only Victoria blue gave only a pale blue coloration. Inks containing Victoria blue and methyl violet yielded a pale blue coloration with vivid purple around the edges of the spot.

It was found that a drop of hydrochloric acid caused the indulin in an indulin-Victoria blue mixture to turn dark violet. The "bleed" into the acid drop, when neutralized with sodium bicarbonate, gave a pale blue coloration indicating the presence of Victoria blue.

The iron blue ink gave a deep red color when a drop of dilute potassium thiocyanate was added to the hydrochloric acid spot on the ink line. False positives resulting from paper impurities and reagent reactions were checked by running controls. The presence of methyl violet was confirmed by neutralization of a second hydrochloric acid spot with sodium bicarbonate, and observing the reconstituted vivid purple coloration.

It was found, with the phthalocyanine based inks, that those containing Victoria blue, methyl violet, and rhodamine B, all "bled" into hydrochloric acid, but those containing alkali blue did not. Phthalocyanine and alkali blue ink produced only a deep green ink line color.

The presence of rhodamine B in an ink was demonstrated by spotting the ink line with N,N-dimethylformamide and observing the ink line under ultraviolet radiation. The resultant bright pink fluorescence was observable under both short

and long wave-length ultraviolet lamps. It was found that the fluorescence of rhodamine B was attenuated somewhat after spotting with hydrochloric acid followed by neutralization with sodium bicarbonate.

Mixtures of phthalocyanine blue and methyl violet gave, with hydrochloric acid, a light green phthalocyanine ink line color and a pale yellow "bleed" into the hydrochloric acid. When neutralized, the spot gave a vivid purple coloration, with an absence of any pale blue coloration in its center.

Mixtures of phthalocyanine blue, Victoria blue, and methyl violet gave a brownish solution in the hydrochloric acid, and the neutralized spot on the filter paper showed a pale blue center with vivid purple on its outer borders.

The phthalocyanine blue and rhodamine B formulations gave a pale yellowish "bleed" into the hydrochloric acid. Upon neutralization, the acid spot on the filter paper was pinkish around the edges, and exhibited a bright pink fluorescence. There was an absence of any indications of Victoria blue or methyl violet.

With phthalocyanine blue, Victoria blue, and rhodamine B formulations, it was found that the hydrochloric acid drop was browner than with rhodamine B alone. The neutralized spot contained a diffused pale blue area with the pink rhodamine B coloration around its edge.

The phthalocyanine blue, Victoria blue, and alkali blue mixtures had a "bleed" into the hydrochloric acid with a pale blue coloration after neutralization. Indications of methyl violet and rhodamine B were negative. While the presence of alkali blue was not demonstrated in this case, it was noted that Victoria blue has not been found alone with phthalocyanine. Therefore, in this case, the presence of Victoria blue, and the absence of a red or purple dye, was indicative of the presence of alkali blue.

Using these spot test observations, a simple scheme for the presumptive identification of the ten known ink formulations was postulated. It should be noted that only dyestuffs expected to be found in blue ballpen ink formulations are covered by this scheme. These dyestuff group reactions should be considered as indications, rather than definitive identifications, of a dyestuff class. From a forensic point of view, they indicate only that ballpen ink "X", for example, gives reactions typical of phthalocyanine blue and rhodamine B.

### Scheme for the Presumptive Identification of Ballpen Ink Formulations

The ink line is spotted with concentrated hydrochloric acid, using a micropipette. The color of the ink line itself and the color of the "bleed," if any, should be observed. When necessary, the hydrochloric acid spot should be absorbed on filter paper and neutralized with saturated sodium bicarbonate solution, and the resultant colors observed. A second spot should be made on the ink line with N,N-dimethylformamide (or other solvents which release the red dye) and then observed under ultraviolet light, either short or long wavelength. All hydrochloric acid spots on the document itself must be neutralized afterwards, to prevent damage to the document. Should aberrant reactions be encountered, conventional chromatography, folfowed by spot testing, should be employed.

1. *Non-phthalocyanine Inks*—absence of greenish or olive color on ink line; no fluorescence.
   a. Indulin and Victoria blue—purple ink line.
   b. Iron blue and methyl violet—positive iron test with KCNS.
   c. Victoria blue—absence of violet coloration after neutralization.
   d. Victoria blue and methyl violet—vivid violet coloration after neutralization.

1. *Phthalocyanine Inks*—greenish or olive coloration of ink line.
   2. *Presence of rhodamine B*—bright pink fluorescence.
      e. Phthalocyanine and rhodamine B—no blue or purple colors after neutralization.
      f. Phthalocyanine, Victoria blue and rhodamine B—purple, blue, and red colors after neutralization.
   2. *Absence of rhodamine B*—no pink fluorescence.
      3. *No bleed in HCl.*
         g. Phthalocyanine and alkali blue.
      3. *Bleed in HCl.*
         h. Phthalocyanine, Victoria blue and alkali blue—no violet coloration after neutralization.
         i. Phthalocyanine and methyl violet—pale green ink line, pale yellow bleed.
         j. Phthalocyanine, methyl violet and Victoria blue—brownish bleed, violet color, after neutralization.

### Chemical Basis for the Spot Tests

The following mechanisms are postulated to explain the color reactions encountered in the outlined spot tests:

a. Alkali blue is acid resistant, and therefore, it is unaffected and insoluble in HCl.

b. Rhodamine B, methyl violet, and Victoria blue are all affected by acids, and the altered form of the dyestuff is soluble in HCl.

c. The acid-base reactions of these dyestuffs are as follows: the addition of HCl to the dyestuff causes the reaction to go from "B" to "C," and the addition of $NaHCO_3$ subsequently causes the reaction to go from "C" to "B." In all cases "A" represents the carbinol form of the dyestuff. (See fig. 1, 2, and 3.

d. Although Fieser and Fieser (16) claim that copper phthalocyanine is "not affected by molten alkali or boiling HCl," and that it can be recovered "unchanged" after solution in concentrated sulfuric acid, Ellis (17) states that "the metals (Cu) may be removed from these compounds (phthalocyanines) by treatment with concentrated sulfuric acid." These viewpoints are not irreconcilable when one considers the semantics of the situation. Some reaction occurs, obviously, when concentrated sulfuric or concentrated hydrochloric acid is spotted on copper phthalocyanine. While this reaction might not produce a total breakdown of the phthalocyanine molecule, it is reasonable that Cu could be removed from the phthalocyanine which is a green pigment (17). This reaction might be produced as shown in figure 4.

### The Comparison of Ballpen Inks

A comparison of the visual appearances of the test inks revealed that: 1. Two inks of different dyestuff constituency can have the same visual appearance, and that 2. Two inks having the same qualitative constituents can have different appearances because of quantitative differences.

Therefore, for two inks to be of the same class, they must both look alike visually, and give the same chemical reactions. The outlined method covers only the qualitative analysis of the dyestuff constituents, and does not give any quantitative measurements. The quantitative differences may be apparent visually.

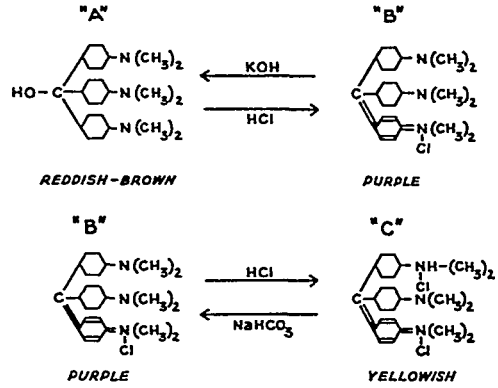


Figure 1—Methyl Violet

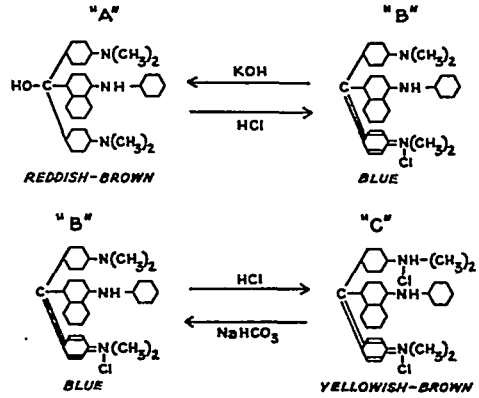


Figure 2—Victoria Blue

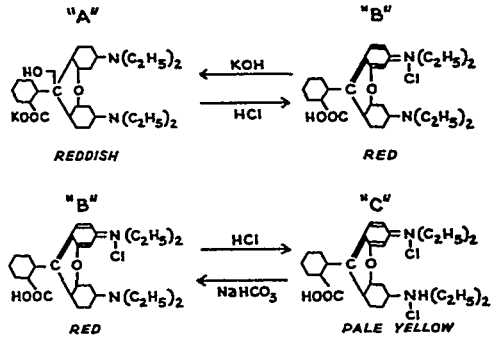


Figure 3—Rhodamine B

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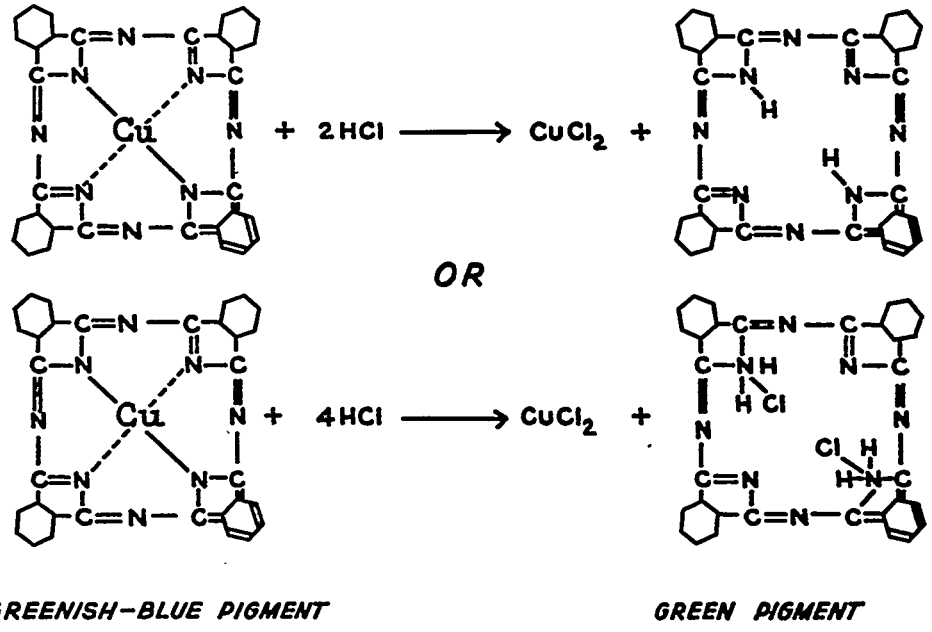


Figure 4

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