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COMPOSITION, PROPERTIES AND BEHAVIOR OF BALL PENS AND INKS

WILMER SOUDER

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The idea of writing with a ball point pen can be traced to the year 1880. Pens were constructed in 1895, and ink was patented in 1898, but little came of these inventions. Between 1935 and 1939 25,000 ball point pens were produced in Europe. In 1943 a European, Biro, took the French patent to the Argentine and started the production of pens. Our military personnel brought this "miracle" pen, which would write under water, to the U. S. A. Produced and publicized by Reynolds in 1946, the pens were exploited and flooded the market.

The exploitation of the public in the sales of assembled parts, untested inks, and non-specific performance tests are typical of numerous similar merchandising methods which the public accepts. Failures and disappointments in so many of these pens gave the item a setback from the annual sales total of about 30 million pens in 1948. Belated research in design, ink, and performance is now bringing the ball pen into favor with those who are bold enough to take a second (or tenth) chance on an item which can, with proper efforts, be produced to give satisfaction.

TECHNICAL DETAILS

The popular diameter of the ball is one millimeter. The clearance between the ball and socket is given as one quarter to five microns. (Metrologists will question the precision of exact values given for such assemblies of ball and socket.) The thickness of the line of ink placed on the surface of smooth paper is supposed to be one tenth to one fiftieth of the thickness of conventional pen writings. The ball pen is essentially a printing device as it presses the thin film ($\frac{1}{4}$ to 5 microns) of ink on the paper. If the ball rolls perfectly, there is no movement between it and the center of the line on the paper. However, there is always more or less slippage by reason of friction in the mounting, viscosity of the ink, and smoothness of the ball and paper surfaces. Pigmented inks and precipitates may disclose this slippage in deposits against fibers in the paper in a manner resembling the patterns produced by soft lead in pencils. Heavy pressure in writing may sink the ball into the paper and produce a wider line. At the edges of the line the slippage is greater than at the center. This greater width of contact may show the sequence of writing across a fold. The convexity of

the fold may extend up along the side of the ball and wipe off more ink than normally is left on a flat surface, thus widening the line at the fold.

Marks of identification for ball pen writing are the "Goop" spots which frequently appear after a curve or sharp change is made in the direction of the line. Such spots result from changes in axes of rotation of the ball. Excesses of ink, scraped from the returning surface of the rotating ball, accumulate at the rim of the ball housing until a reversal of direction pulls them away and deposits them at the edge of the line. From these spots it is possible to determine the direction of motion of the pen.

Ball pen ink can be as simple as lampblack pigment ground in castor or mineral oil to a fineness of particle size less than the clearance of the ball and socket. The next step might be the addition of oleic acid to improve the fluidity and wetting properties. The substitution of a dye for the pigment might free the action from clogging. Here the choice will be among the water, spirit, and oil soluble dyes; some basic, others acid. The vehicle must be compatible with the dye. Some dyes must be sulfonated before they will combine with the vehicle. If resins are used such as polyvinyl chloride or polyvinyl acetate, it may be necessary to use glycol ester to keep them in solution.

PAPER AND INK

Cellulose (paper) is not satisfactory as a surface to accept ink until it is sized and calendered with resin, glue, starch, or similar material to prevent feathering. The sized surface may have a pH value of 4 or 5, definitely acid. A basic ink on the acid surface may neutralize the size and feather in the cellulose. Soluble wax or resin in the ink may correct or reduce this defect. The basic dyes combined with phosphomolybdic and tungstic acids are said to produce the best inks. Dyes combined with the oleates do not wet the ball so well as other combinations. The oleates may attack the ball or dry in spots on the ball.

Formulas for dyes which are satisfactory in these inks are not too plentiful. Among those mentioned are: Victoria blue and green, rhodamine red, nigrosine black, methyl orange, methyl violet, congo red, para red, aniline, and phthalocyanines. Basic dyes are less permanent. Acid dyes usually are mixtures and must be sulfonated to make them combine with oils.

Nickel, chromium, copper, and other metallic salts may be found in some inks. Stainless steel balls may replace the conventional hardened steel balls. Sapphire balls are used by one firm. This aluminum oxide gem should carry the ink better than the polished metal ball.

DIFFERENTIATION

The identification of an ink may sometimes be rather simple if a few milliliters are available. It may be possible to layer it with sodium hydroxide and ether solutions. The layers may be drawn off and deposited on filter paper for spot testing with acids, alkalies, etc. Pigments may be centrifuged into a layer. With the small amount of ink in a ball pen line such procedures are impossible. Spot testing on a surface of the paper is the most practical. A limited amount of color separation

(chromatogram) may be produced by the test chemical after it has attacked the ink, if it is spread with a glass rod.

The use of the stereoscopic microscope, ultraviolet light, camera, filter, and special films are the preferred instruments for showing differences in inks on documents as they produce the least permanent change or injury to the document.

If spotting must be tried, the following chemicals should be helpful:

Water

Methyl "Cellosolve" (Ethylene glycol monomethyl ether)

Trichloroacetic acid 25% and 5%

Sodium hypochlorite (acidified) about 5%

n-Butanol

Nitric acid about 5%

Acetic acid about 5%

Sodium hydroxide about 5%

Ethyl acetate

Ethylene glycol (takes 24 hours to dry).

There are numerous precautions which must be observed as some of the chemicals are powerful, (attack the paper), some spread rapidly, and some dry very slowly. A microdropper is necessary.

Two satisfactory microdroppers may be made from an eight centimeter length of ordinary five millimeter (outside diameter) glass tubing. Heat the center section until it softens and pull the tube to a length of 20 centimeters. Cut out part of the center section leaving two droppers about six centimeters long. Attach a 5 centimeter length of soft rubber tubing to each dropper. Plug the open end of the rubber tube with a short piece of glass rod (or a BB shot).

SEQUENCE

Determination of sequence of crossed lines may sometimes be established if the ink flow is heavy, the ink colors are different, and the pressure is heavy. Obviously, these *ifs* depend upon laying (printing) a film of contrasting ink over a writing of different color, a penciled, or typed character. Pencil writing over the ball writing may scratch the ball-printed film and thus disclose the sequence, just as conventional pen nibs may cut the film. Keen examiners will have friends prepare secret sets of crossed lines of ball pen inks, graphite pencils, type, and stamp inks. Studies of these specimens will be of great value to the examiners. They will soon discover that the pencil deposits placed first on the paper frequently will cause the ball to skid or fail to overlay the graphite with ink. If the ball does overlay the graphite with ink, the relative thinness of the ink film (perhaps only a few microns) may not be sufficient to hide the heaps of graphite (perhaps 100 microns high). The best stereoscopic microscope obviously will show many mirrorlike particles of graphite on top of or projecting through the thin ribbon of ink.

If a writer attempts to place (write) the graphite pencil line over the dry ink line, he may find the graphite failing to deposit on the ball pen ink lines which are from some pens more like a varnish or floor wax.

In cooperation with Mr. W. J. Barrow, document restorer of the Virginia State Library, an attempt was made to separate or split the top layer from the bottom layer of crossed lines. Every attempt failed until Mr. Barrow suggested pressing or ironing an area of blank paper over and in contact with the crossed lines. Graphite, if on top of an inked line, should transfer to the blank paper. If under a sufficiently heavy coating of ink it should not transfer to the blank sheet. In most instances the opposite types of transfer were observed. This indicates the pencil may skid over the ink and the ball may skid over the graphite. For three higher priced pens used this was uniformly true. All writings must be made over well dried inks, and pressings must be delayed until the inks are completely dry. Convincing tests may be made by techniques as simple as placing the document on a smooth, hard surface, covering the crossed lines with a small sheet of blank paper, and rubbing or ironing it with the rounded edge of a bone spatula, the edge of a thumb nail, or other blunt tool. The ironing should be done with about 100 rotating strokes, and the blank paper must not move in relation to the document bearing the writings. Permission should be obtained, and witnesses should be present if such tests are made on questioned documents.

Equally searching experimentation and rigorous analyses are necessary when crossings of type ribbon, stamp pad, conventional, and ball pen inks are encountered.

PERMANENCE

Deterioration of ball pen inks, by exposure to light, may no longer be a serious problem if the pen bears the name or brand mark of a reliable manufacturer. Ball point pens appear to be on a rebound and may now establish their place in industry on a basis of merit. Such pens will not sell for 20 cents each.

Twelve specimens of writings, from currently available ball pens, were exposed to an American Optical Company Hague Ultraviolet lamp for two hours at a distance of 30 centimeters. No fading was discernible.

These specimens were also spot tested with the ten chemicals listed in the section above, labeled *Differentiation*. In not more than one instance was the ink completely eliminated. What more may we ask in permanence? Benk states: "Ball point pen inks are superior in permanence to fountain pen inks".

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PATENTS

BALL POINT PEN INKS

U. S. 2427921 9/23/47		U. S. 2585531 2/12/52 (perfumed)	
Pfaelzer to Milton Reynolds		Bernfeld, Bomse & Scharfsplitz	
Methyl violet	0.72 parts	Water	4800 to 5000
Victoria blue	1.68	Stearin	50
Oleic acid	2.42	Glycerin	50
Mineral oil	0.84	Triethanolamine	100
<hr/>		Lanolin	100
Hung. 138248 1/2/48 Biro		Tolu balsam	20
Glue, dextrin or polysaccharide plus glycerol or cholesterolized oil containing dye		Muscione	30
<hr/>		Ambrette	50
Japan 181080		Patchouli	50
Vinyl chloride resin	30	Cholesterol	2
Ethylene glycol	40	Styrax gum	50
Oil soluble pigment	30	Aniline color (blue, brown, red or the like)	400
<hr/>		Alcohol q s	6000
Japan 181084		U. S. 2623827 12/30/52 (thixotropic)	
Oxidized castor oil plus 2% polyvinyl acetate in glycol ester plus oil soluble pigment		Moos to Eversharp	
<hr/>		Victoria blue oleate	56
Japan 181391 1/16/50		Carbowax 1500 plus polyoxy- ethylene glycol 400	15
Methyl or ethylricinoleate plus a dye or pig- ment		Victoria blue phospho- tungstic toner (pigment)	27
		Tween 20 (surface active agt)	2