COLOR CHANGING PENS

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You have seen them at shopping malls, airports, specialty shops, and in most store selling stationary supplies. Sometimes called Magic Pens, they are color changing markers, often marketed at a high price by a person who, with great flair, demonstrates their capabilities at a small booth or cart to a crowd. They are also available off-the-shelf in most stationary and novelty stores under the Crayola® name and, also, at a more reasonable price.

Binney & Smith, the makers of Crayola®, produces two types of markers, Changeable™ Color Change Markers and OVERWRITERS™ Color Over Color Markers.

Changeable™ Color Change Markers consist of a set of six color markers and two Color Change Wands (see Table 1). To use them, you simply write and/or draw on your paper with the color markers, allow them a few seconds to dry, and use the Color Change Wand to change the bright color to a new color. The Color Change Wand can also be used to write an invisible message that can later be developed by writing over it with a Changeable™ marker.

Table 1. Colors of Changeables™ Markers (initial color to changed color)
Black to orange
Purple to coral
Blue to aqua
Green to purple
Yellow to fuchsia
Red to goldenrod

The component inks are a combination of two dyes, one that is stable in low pH of about 4 or less and one that is stable at high pH of about 10 or above or in the presence of a reducing agent such as sodium sulfite, Na_2SO_3, or sodium metabisulfite, $Na_2S_2O_5$. Such dyes are called erasable inks. Suitable dyes are polymethine dyes, which contain a series of –C= groups connected to the terminal groups of the chromophore (the color producing part of the molecule), and azo dyes, which are characterized by the presence of one or more –N= groups.

Black ink is a mixture of several dyes. The black ink was separated by paper chromatography using water as the solvent. Although only a fair separation of inks occurred, the black ink appears to be a mixture of blue, yellow, and red inks, but not the same inks used in the acid colors of the pens. Chromatographic separations of individual pen colors are left as an exercise for the interested reader.

The ink composition in the markers consists of deionized water as the solvent, a highly polar glycol such as ethylene glycol, diethylene glycol, or triethylene glycol as humectant to keep the wands from drying out, a non-sudsing detergent as a wetting agent, citric acid as an antioxidant, and the dye. The Color Change Wand contains a solution made from deionized water, a highly polar glycol, a non-sudsing detergent, and, for maximum effect for the color change, a reducing agent such as sodium sulfite, Na_2SO_3, or sodium metabisulfite, $Na_2S_2O_5$ in combination with a base such as sodium hydroxide, NaOH.

pH testing was done using Alkacid® Test Paper. No measurements could be made using the Changables™ markers as the colors of the inks masked the results on the test paper. The Color Change Wand, which contains a colorless solution, did indicate a pH of 10 or above.

The Changables™ pens were tested to determine the effects of oxidizing agents, reducing agents, base, and acid on the inks by applying solutions of 3% hydrogen peroxide, Chlorox bleach, 0.1 M sodium sulfite solution, 0.1 M sodium carbonate solution, 1 M sodium hydroxide solution, and 1 M hydrochloric acid solution to samples of the

inks on standard bond paper by use of cotton swabs. Care was taken to avoid excess liquid from dissolving inks. The results are listed in Table 2.

Table 2. Effects of oxidizing agents, reducing agents, base, and acid on Changables™ inks

Compound used	Effect
3 % hydrogen peroxide	Weak bleaching effect on black, purple, and blue inks
Chlorox bleach	Bleaches all color in inks
0.1 M sodium sulfite	Changes color of all inks
0.1 M sodium carbonate	Color changes, best in black, purple, and blue inks
1 M sodium hydroxide	Changes color of all inks with only partial change of red ink.
1 M hydrochloric acid	No effect

OVERWRITERS™ Color Over Color Markers consist of a set of four Under Color Markers and four Over Color Markers (See Table 3). To use them you write and/or draw with the Under Color Markers and then color over the base colors with the Over Color Markers. These markers allow you to color four colors over any of the base colors as opposed to the two color change that you are limited to with the Changeable™ Color Change Markers.

Table 3. Colors of OVERWRITERS™ Markers

Under Color Markers	Over Color Markers
Black	Light blue
Blue	Light green
Green	Yellow
Red	Pink

The components of the OVERWRITERS™ Under Color Markers consist of two types of acid stable erasable dyes. One type, polymethine dyes, which contain a series of –C= groups connected to the terminal groups of the chromophore, are used for blue, red, or pink colors. The second type are azo dyes, which contain one or more –N= groups, are used for green or violet colors. The black ink was found to be a mixture of blue, green, red, and yellow inks by using paper chromatography with a water solvent. Chromatographic separations of individual pen colors are left as an exercise for the interested reader.

The components of a typical maker used for the under color are a dye, deionized water, glycerin as a humectant, ethyl alcohol as a drying agent, and a preservative to inhibit growth of bacteria and fungi.

The components of the OVERWRITERS™ Over Color Markers consist of xanthene dyes, commonly used for foods, drugs, and cosmetics, which are stable in acid and alkaline solutions (The structure of eosine I bluish, a typical xanthene dye, is shown in Figure 1.), a bleach to erase the under color, a base to increase the pH to 10-12, glycerin, as a humectant, and ethyl alcohol as a drying agent. The bleach that is used is sodium sulfite, Na_2SO_3, although other bleaches that can be used are sodium hypochlorite, NaClO, hydrogen peroxide, H_2O_2, and hydrogen sulfide, H_2S. The base that is used is usually sodium hydroxide, NaOH, although sodium carbonate, Na_2CO_3, or aqueous ammonia solution (ammonium hydroxide, NH_4OH) can be used.

The bleach, along with the base, erases the color of the under color ink. To test the effects of bleaches, base, and acid on the OVERWRITERS™ inks, a laboratory experiment was conducted by applying solutions of 3% hydrogen peroxide, Chlorox bleach, 0.1 M sodium sulfite solution, 0.1 M sodium carbonate solution, 1 M sodium hydroxide

solution, and 1 M hydrochloric acid solution to samples of the inks on standard bond paper by use of cotton swabs. Care was taken to avoid excess liquid from dissolving inks. The results are listed in Table 4.

Table 4. Effects of bleach, base, and acid on OVERWRITERS™ inks

Compound used	**Effect on Under Color Inks**	**Effect on Over Color Inks**
3 % hydrogen peroxide	Weak bleaching effect	Little or no effect
Chlorox bleach	Bleaches color	Bleaches color
0.1 M sodium sulfite	Bleaches color	No effect
0.1 M sodium carbonate	Weak bleaching effect	No effect
1 M sodium hydroxide	Medium bleaching effect	No effect
1 M hydrochloric acid	No effect	No effect

pH testing was done using Alkacid® Test Paper. No measurements could be made using the under colors as their colors masked the results on the test paper. The over colors, however, did indicate a pH of 10 or above with the dark color of the pH paper showing through the colors of the inks.

As a result of this investigation, it is apparent that there is no *magic* in Magic Pens, just some acid-base reactions along with some oxidation-reduction bleaching.

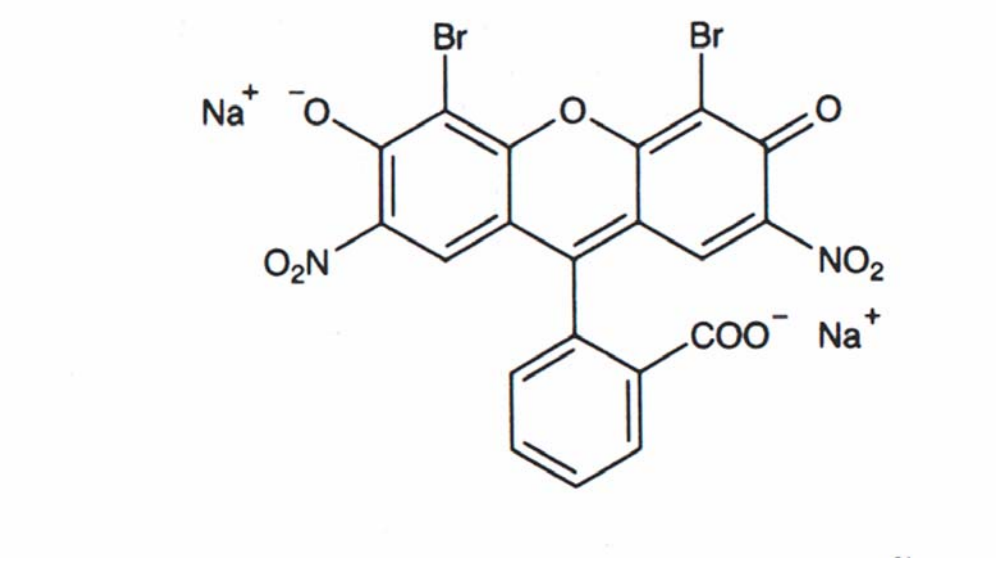

Figure 1. The structure of eosine I bluish