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Thiazine, Oxazine, and Phenazine Leuco Dyes

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3.1. INTRODUCTION

Benzoyl leuco Methylene Blue (1), which is a phenothiazine leuco dye, has been known since 1900. The material was developed to extend the range of hues and colors obtainable in such applications as pressure-sensitive carbonless paper and to complement other classes of leuco dyes such as triarylmethanes, crystal violet lactone, and fluorans. Benzoyl leuco Basic Blue 3 (2), which is a phenoxyazine leuco dye, is a more recent development.

New applications have recently emerged, spurring the need for the development of new leuco dyes including leuco phenazine dyes: electrolytic
recording paper, transparencies for overhead projector, thermographic and photothermographic materials also known as Color Dry Silver.

### 3.2. THIAZINE LEUCO DYES AND APPLICATIONS

When Methylene Blue is reduced, the yellowish leuco cannot be isolated due to instant air oxidation. Benzoylation of the leuco form provides stabilization. There are also leuco thiazine dyes stable enough to be isolated without the need for aroylation.

#### 3.2.1. Acylated Leuco Thiazine Dyes

There are cationic thiazine dyes (3 to 5) and neutral thiazinone dyes exemplified by Methylene Violet (6). Like leuco Methylene Blue, leuco Methylene Violet is too air sensitive to be isolated and therefore requires acylation.

![Chemical structures](image)

(3) AzureA  \( R^1-R^2=H \)

(4) AzureB  \( R^1=H; R^2=CH_3 \)

(5) Methylene Blue  \( R^1=R^2=CH_3 \)

(6) Methylene Violet

#### 3.2.1.1. Acylated Leuco Cationic Thiazine Dyes

The leucos 7a–d are described as useful in printing ink for preventing forgery, whereas 7e–g are used in pressure sensitive copying paper.

The leucos 7h–o are claimed in electrolytic recording paper using a process coined “electrochromic recording” which is an irreversible electrooxidation of the leuco dye to regenerate Methylene Blue, not to be confused with reversible electrochromic display. The process consists of passing an electrical pulse through a substrate containing the leuco dye and